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Indium iodides †

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Indium iodides have been studied for more than a century, the focus of scientific interest being shifted from inorganic compounds, components of fluorescent metal halide lamps, to complexes and (in the current century) organoindium compounds. The review surveys the properties of individual iodides, phase diagrams of systems involving InI_3, InI_2 and InI, structural data and complex compounds of indium iodide. Some discrepancies in the published data are noted. The existence of new compounds that are yet to be described is predicted. Indium monoiodide and its derivatives are of interest as materials for radiation detectors and infrared photonics. The physical and chemical problems of application of indium iodides in metal halide lamps are considered. A detailed review of patents on this topic is given. Chemical reactions involving indium iodides that are used in organic synthesis and the types of organoindium compounds thus formed are discussed.
The bibliography includes 316 references.

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I. Introduction

Indium iodides have been known for more than a century. Indium iodide was synthesized for the first time by Meyer [1] in 1869 *via* the reaction of indium metal with iodine under CO_2 atmosphere six years after the discovery of indium by Reich and Richter.[2] The correct formula — triiodide InI_3 — was proposed once Mendeleev had assumed indium to be trivalent.[3] Mono- and diiodides were discovered by Thiel and Koelsch [4] in 1910 when they studied the In—I system.

The chemistry of indium iodides has attracted interest in recent years for several independent reasons. The ability of indium to change its oxidation state offers great opportunities for using organometallic compounds of this element in modern organic synthesis.[5–8] Numerous studies were concerned with the application of indium tri- and monoiodides along with other indium derivatives in metal halide lamps. Indium monoiodide (InI) has such benefits as high light output, good stability, low hygroscopicity (which is a rare case for iodides), low toxicity and the possibility of growing large single crystals of this compound, due to which it has received attention in recent years as a promising material for radiation detectors [9–13] and an infrared optical material.

The possibility of producing an optical material and prospects for its practical applications are governed by a number of factors, such as chemical stability (especially

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against water and oxygen), mechanical properties allowing for the optical treatment of the surface, thermal stability and the availability of an appropriate method for the synthesis of a single- or polycrystalline material. Construction materials for IR optics (barium fluoride, potassium chloride and bromide, caesium iodide, germanium, single- and polycrystalline zinc chalcogenides, solid solutions of thallium halides [14, 15]) have specific drawbacks (hygroscopicity, or near IR absorption edge, or insufficient light transmission, or toxicity), while indium monoiodide is free from these disadvantages.

In recent years, heavy metal halides have attracted interest as promising materials for new efficient scintillators.[16] In quantum electronics, metal iodides are very attractive as laser matrices for rare-earth elements due to 'short' phonon spectra that prevent the development of the adverse effect of multiphonon relaxation. This provides opportunities for the design of new laser materials for radiation generation not only in the near-IR but also in the mid-IR region.[17]

Chemistry of indium iodides is considered in general monographs on indium and its halides [2, 18–24] and also on metal iodides.[25] The reviews [5–8, 26–28] are of particular notice. However, the monographs have been published quite a long time ago and are somewhat obsolete. The exception is the monograph by Fedorov and Akchurin;[24] however, not all of the published literature was summarized because of limitations of the print monograph. Besides, extensive new data have been published since then. All of the reviews were devoted to certain areas of chemistry. In particular, the review written by Shen *et al.*[8] was concerned with general aspects of chemistry of organoindium compounds. The detailed consideration of organic indium iodides was beyond the scope of this review (the authors discussed only some studies dealing with the chemistry of organoindium derivatives), nothing to say about the properties of inorganic and complex organic indium iodides.

Figure 1 presents the evolution in the number of publications on indium halides over time.

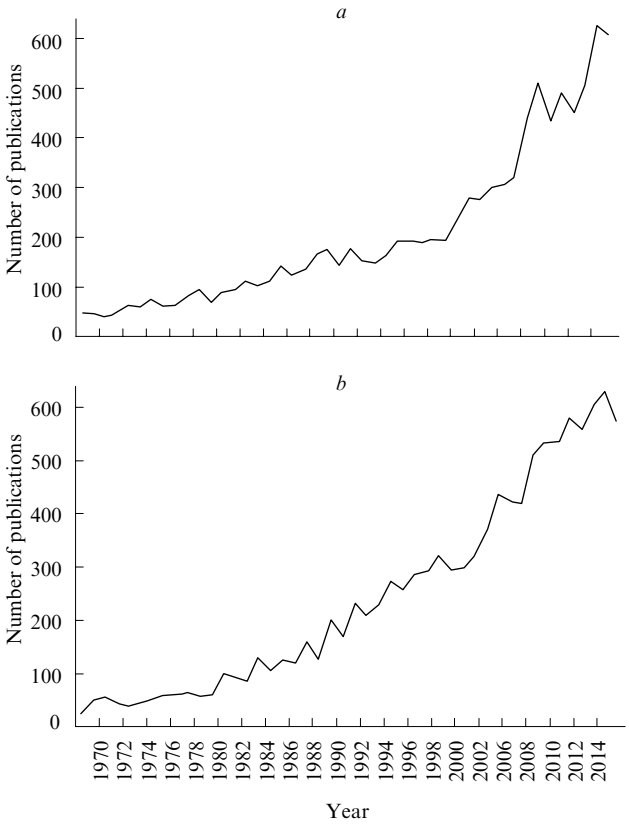


Figure 1. Evolution of the number of publications on indium compounds per year according to the Web of Science database (All Databases).
(*a*) Search using the keywords indium* and (halide or halogen or fluoride or chloride or bromide or iodide); (*b*) search using the keywords indium* and complex*.

II. Physicochemical properties of indium iodides

The phase diagram for the indium–iodine system was studied for the first time by Thiel and Koelsch [4] in the region from 50 at.% to 75 at.% iodine and then more comprehensively by Peretti.[29] Three congruently melting compounds, namely, indium mono-, di- and triiodides, formed in the indium–iodine system (Fig. 2).

Highest-purity indium triiodide can be synthesized from the elements by heating a mixture of the metal with iodine in an evacuated and sealed ampoule. Another method for the synthesis is based on the reaction of the metal with a iodine solution in such solvents as benzene,[30, 31] diethyl ether,[32] butyl iodide,[33] xylene,[34] carbon disulfide [35] and so on. Upon cooling or evaporation, triiodide crystals precipitated from the solution. After the filtration and washing, the crystals need to be dried over P_2O_5 and paraffin wax (to absorb solvent vapour). Indium iodide can also be prepared by dissolution of hydroxide in an aqueous HI solution followed by evaporation of the solvent.[24, 26, 36]

Indium triiodide can be purified, in particular from lower iodides, by vacuum sublimation or distillation.[37] Besides, InI_3 can be purified by recrystallization from

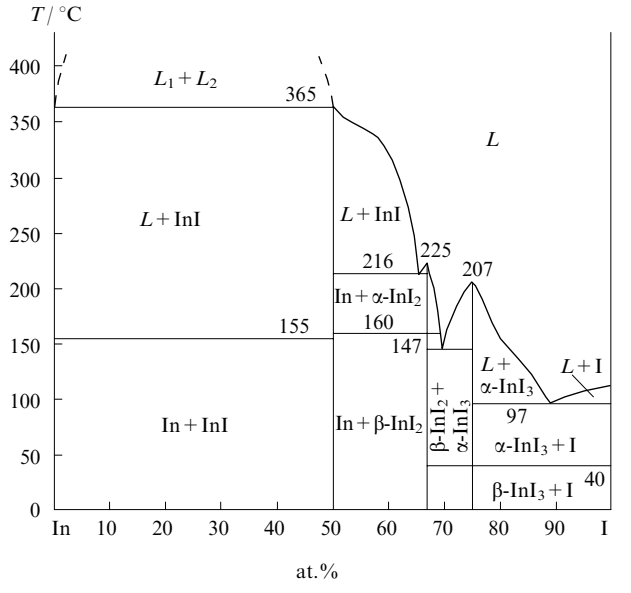


Figure 2. Phase diagram for the indium–iodide system taken from Peretti [29] with supplements.
L is liquid.

anhydrous diethyl ether or another solvent.[24,26] The zone melting technique has proved to be successful in the purification of InI_3.[38]

Indium mono- and diiodides can be synthesized by the reaction of indium with iodine in a sealed ampoule,[39–41] by melting triiodide and making it to react with indium metal[37,42] or its reduction with hydrogen and also by melting together indium and mercuric iodide in a sealed evacuated ampoule. The reaction of indium metal with anhydrous ammonium iodide is a method of choice for the synthesis of monoiodide.[23,43]

$$2\,In + 2\,NH_4I \longrightarrow 2\,InI + 2\,NH_3\uparrow + H_2\uparrow$$

Grinberg *et al.*[44] initially performed the reaction of the elements to prepare nonhygroscopic indium monoiodide, which can be easily purified by sublimation, and then synthesized tri- and diiodides by the reaction of InI with iodine. Ichikawa and Ikawa[37] prepared diiodide by fusing together mono- and triiodides *in vacuo* at 220–230 °C. Freeland and Tuck[34] synthesized InI_2 by the reaction of a solution of InI_3 in xylene with indium metal or indium monoiodide.

Indium monoiodide can be efficiently purified by means of crystallophysical purification techniques (zone melting or directed crystallization of a melt). Denisov *et al.*[45] determined the distribution coefficients of Ag, Cu, Sn and Ni impurities for the directed crystallization of InI in a series of studies,[9,11–13] the zone melting was used for the purification of indium monoiodide from impurities prior to the single crystal growth. Onodera *et al.*[12] performed multi-pass zone refining up to 80 times at a furnace movement speed of 5 mm h^{-1} along an ampoule approximately 400 mm in length. Brumleve *et al.*[41] employed the filtration of a melt through a quartz filter. Nevertheless, the vacuum distillation is the most efficient method for the purification of the monoiodide.[37,46]

Two modifications of indium triiodide were ultimately established. Classical methods of synthesis produce the yellow α-modification ‡ (Refs 33, 36, 47, 48). The modification α-InI_3 is transformed into the red β-modification after storage in the dark for several weeks. This transition proceeds very slowly and is accompanied by a change in the colour from pale- to dark-red.[36,47] The transformation is not observed when α-InI_3 is stored under daylight. A decrease in the temperature[33] and elevated pressure[23] accelerate the transformation. Chusova[49] synthesized the β-modification by recrystallization of InI_3 from butyl iodide at 0 °C. The red modification is again transformed into the yellow one upon heating. The transition is kinetically hindered. The transition temperature was estimated as 69,[36] 40,[47] 57,[48] 23 °C.[39] Smirnov, Dmitriev and co-workers[23,50] demonstrated that the transition temperature depends on the purity of the iodide. Besides, the lowest transition temperature (40 °C) was observed for the strictly stoichiometric composition, while any deviation from stoichiometry led to a substantial increase in its value (Fig. 3). It is also possible that the transition conditions depend on the dispersity.

‡ By α we denote high-temperature modifications as opposed to, for example, Kniep and Blees[48] (see Fig. 4 below).

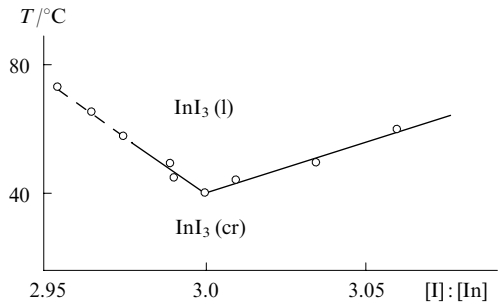


Figure 3. Influence of the I : In ratio on the temperature of the polymorphic transition in indium triiodide.[50]

Heat capacity measurements for InI_3 performed by Chusova[49] demonstrated that there is yet another low-temperature phase transition, which is similar to a second-order phase transition, at 93 ± 2 K (−180 °C) with an enthalpy of 1.2 J mol^{-1}. There is also unsupported evidence reported by Guliev[51] that InI_3 undergoes a phase transition at 126 °C.

The crystal structure of the yellow modification of indium iodide, α-InI_3, was studied by Forrester *et al.*[52] (Table 1). They demonstrated that iodine atoms form a nearly ideal cubic close packing, in which each pair of indium cations occupies two adjacent tetrahedral voids. The Raman spectra of this modification are indicative of the existence of dimeric molecules In_2I_6 in the solid state.[42]

In order to study the structure of the red modification β-InI_3, Kniep and Blees[48] grew a single crystal of the solid solution $In(I_{1-x}Br_x)_3$ ($x = 0.33$) from a melt. The conditions for the crystal growth were chosen based on the phase diagram (Fig. 4).

The red modification β-InI_3 is isostructural with the low-temperature modification of $CrCl_3$. The structure of this modification can be described as a nearly regular hexagonal close packing of anions, in which cations occupy 2/3 of octahedral voids in an ordered fashion.[48] A change in the crystal structure is accompanied by changes in the Raman spectra.[42]

It should be noted that, as can be seen from a graphical representation,[85,86] the X-ray diffraction pattern of a sample (lemon-yellow crystals corresponding to the formula InI_3 according to the results of chemical analysis) that was prepared from a benzene solution[87] and that was investigated by Dudareva and co-workers[85–93] differs from the X-ray diffraction patterns of both the yellow[52] (JCPDS card 73-0715) and red[47,48] modifications of InI_3. The melting point of this sample (198 °C) is somewhat lower than that of the stable yellow modification. The vapour pressure above the melt of this phase[90] is consistent with the data on the vapour pressure of InI_3 obtained by other authors (Fig. 5). This excludes substantial contamination of the sample. Apparently, this synthetic approach[87] affords another, presumably metastable, modification of InI_3. The X-ray diffraction pattern of this modification is presented in Table 1 in the electronic supplementary information (see iopscience.iop.org/journal/0036-021X).

When melted, InI_3 is transformed into a dark-brown liquid. Wood and Ritter[98] interpreted the X-ray diffraction data for liquid indium triiodide as the coexistence of monomeric and dimeric molecules in the melt. Klemm[99]

Table 1. Properties of indium iodides.

Formula	Crystal system, space group, structure type	Lattice parameters				Z	ρ /g cm^{-3}		Ref.	Melting point (decomposition temperature, polymorphic transition temperature) /°C	Colour
		a /Å	b /Å	c /Å	β /deg		experiment	X-ray diffraction data			
α-InI_3	Monocl., $P2_1/c$	9.837	6.102	12.195	107.69	2	4.70	4.72	52	208 (see [29])	Yellow
β-InI_3	Rhomboh., $R3$	7.229		20.514		6	5.20	5.32	48	40 (p.t.) [47, 50]	Red
$InInI_4$	Orthorh., $Pnna$, $GaCl_2$ type	8.425	10.969	11.162		4	4.71	4.75	53, 54	–	Yellow
$InInI_4$	Orthorh., $Pncm$	8.483	11.020	11.246		9	–	5.24	55	–	–
InI	Orthorh., $Cmcm$, TlI type	4.763	12.781	4.909		4	5.44 (see [56])	5.37	57, 58	365 (see [56])	Dark-red
$LiInI_4$	Monocl., $P2_1/c$, $LiAlCl_4$ type	8.389	7.512	15.267	92.67	4	–	4.35	59	–	Yellow
$NaInI_4$	Monocl., $P2_1/c$, $LiAlCl_4$ type	8.521	7.661	15.583	92.65	4	–	4.22	60	–	–
$KInI_4$	Cubic, $F\bar{4}3c$, $KTlI_4$ type	19.908				24	–	3.34	59	–	Yellow
$RbInI_4$	Rhomboh., $R3c$	24.526		9.786		18	–	4.15	59	–	Yellow
$CsInI_4$	Monocl., $P2_1/c$, $CsTlI_4$ type	7.384	18.757	8.536	105.75	4	–	4.41	59	–	Yellow
$(NH_4)InI_4$	Orthorh., $Pnna$, $GaCl_2$ type	8.601	11.186	11.363		4	–	3.89	61	–	–
$AgInI_4$	Hex., $P63mc$	17.536		7.218		8	4.99	5.05	40, 62	253 (see [40])	–
$InI_3 \cdot TeI_4$ (see [a])	Orthorh., $Pna21$	14.752	7.192	23.39		8	–	4.82	63	165 (see [64])	Black
$(NH_4)_2[(AuI_4)(InI_4)]$	Orthorh., $Pnma$	12.587	20.606	7.696		4	–	4.54	65	–	Black
$(Bi_8)_3Bi[InI_4]_9$	Cubic, $Fm\bar{3}c$	20.162				3	–	5.8	66	–	Black
$AgInI_2$	Tetrag., $P4/nmm$	8.403		7.575		4	–	5.92	40, 67	209 (inc.) [40] 220 (inc.) [68]	Dark-chestnut
$AgIn_2I_3$	Rhomboh., $R\bar{3}m$, $AgTl_2I_3$ type	10.470		19.870		9	–	5.69	40, 69	252 (inc.) [40] 272 (inc.) [68]	Chestnut
In_4CdI_6	Tetrag., $P4/mnc$	9.060		9.754		2	–	5.53	70	320 (m.p.) [71] 208 (p.t.)	Dark-purple
In_4MgI_6	Tetrag., $P4/mnc$	8.967		9.868		–	–	–	72	–	–
In_4TiI_6	Tetrag., $P4/mnc$	8.954		9.935		–	–	–	72	–	–
In_4CrI_6	Tetrag., $P4/mnc$	9.008		9.723		–	–	–	72	–	–
In_4MnI_6	Tetrag., $P4/mnc$	8.981		9.868		–	–	–	72	–	–
$InSn_2I_5$	Tetrag., $I4/mcm$	8.810		15.24		4	–	5.54	73, 74	290 (see [75]), 300 (see [71])	Red
In_3SnI_5	Monocl., $P2_1/c$	8.869	8.959	17.524	99.33	4	–	5.31	76	270 (inc.) [71, 75]	–
$InSr_2I_5$	Monocl., $P2_1/c$, $NH_4Pb_2Cl_5$ type	9.982	8.914	14.24	89.99	4	–	4.85	77	–	Grey-brown
$InPb_2I_5$	Tetrag., $I4/mcm$	8.908		15.137		4	–	6.43	77	–	Red-brown
$InAlI_4$	Monocl., $P2_1/m$, $Ba_2Zn_2ClF_7$ type	7.135	11.822	11.083	96.32	4	–	4.64	78	194 (see [79])	–
InOI	Orthorh., $Pmmn$	4.05	3.71	9.49		2	6.18	6.0	80	320 (decomp.) [81]	Yellow-green
InSI	Tetrag.	18.28		9.69		32	–	–	81, 82	–	Yellow
InSeI	Tetrag., $I4_1/a$	18.618		10.094		32	–	4.87	83	499 (see [83])	Yellow
InTeI	Monocl., $P2_1/a$	8.407	7.731	8.076	117.03	4	–	5.25	83	467 (see [83])	Red-brown

Note. Z is the number of formula units per unit cell, p.t. is a polymorphic transition, inc. is incongruently, decomp. is decomposition.
[a] A metastable compound.

measured the temperature dependences of the density, viscosity and electrical conductivity of molten indium triiodide. More recently, Schoneborn [100] revised the dependence of viscosity of InI_3 in the range of 280–560 °C: $\eta = 14 \times 10^3 \exp(4.8/kT)$. The specific conductance of the melt varies from 0.054 Ω^{-1} cm^{-1} at 221 °C to 0.096 Ω^{-1} cm^{-1} at 372 °C.[99] Grantham and Yosim obtained similar values.[101]

The vapour pressure of InI_3 was measured by several research groups.[49, 94–97] These data are in good agreement with each other (see Fig. 5).

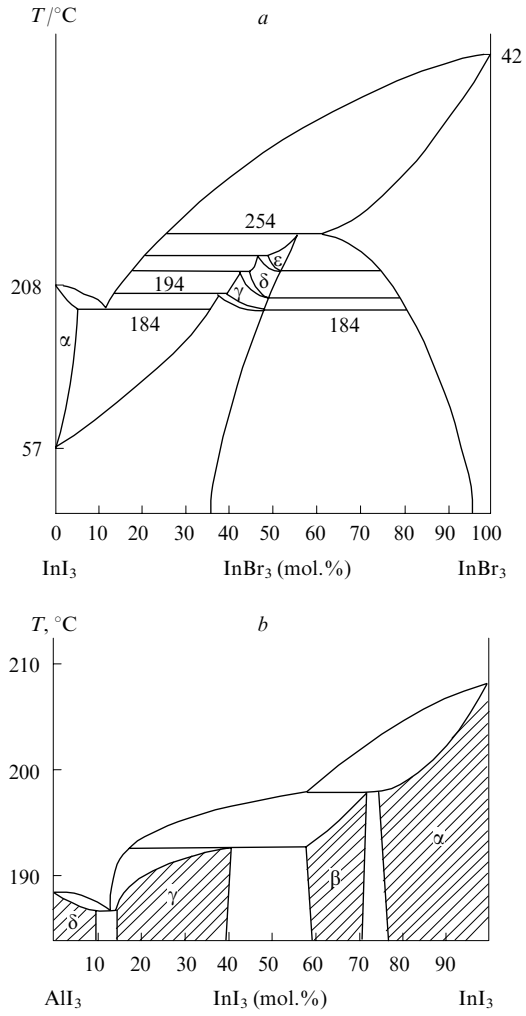


Figure 4. Phase diagrams for the InI_3-InBr_3 (Ref. 48) (*a*) and InI_3-AlI_3 systems[84] (*b*).
Hereinafter, phases of variable composition are denoted by Greek letters.

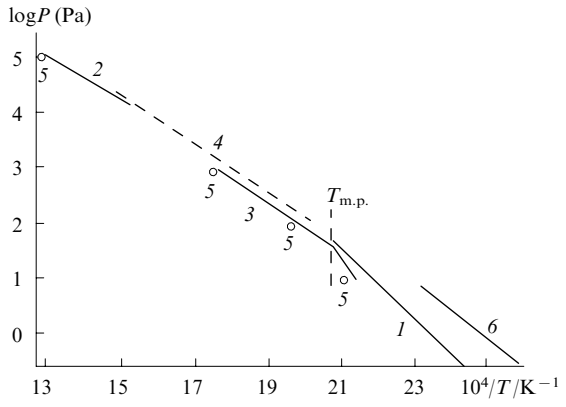


Figure 5. Vapour pressure of indium triiodide according to different authors.
(*1*) Brunetti *et al.*,[94] (*2*) Chernyaev *et al.*[95] (*3*) Fedorov *et al.*[90] (*4*) Chusova,[49] (*5*) Brewer,[96] (*6*) Bencze *et al.*[97]

According to mass-spectrometry data, InI_3 evaporates congruently.[97] The results of electron diffraction studies (Brode,[102] Stevenson and Schomaker[103]) suggest the dimerization of molecules in the gaseous state; the dimers can be described as edge-sharing double tetrahedra like Al_2I_6 molecules. Apart from the dimeric molecules, the vapour contains monomeric iodide molecules and products of their dissociation. Giricheva *et al.*[104, 105] reported that at 190 °C, the vapour of indium triiodide is composed of 80% of InI_3 and 20% of the dimers In_2I_6. At 436 °C, the vapour consists mainly of planar InI_3 molecules. According to the data reported by Titov *et al.*,[106] the temperature dependence of the equilibrium constant for the dissociation of dimers into monomers is described by the following equation:

$$\ln K_p = 36.127 - 12875/T - 2870.4/T^2 - 2.0041 \ln T + 2.84 \times 10^{-6} T$$

These authors also determined the corresponding dependences for the equilibrium constants for two other reactions:

$$In_2I_4 = InI_3 + InI$$

$$\ln K_p = 32.260 - 16910/T + 9903.9/T^2 - 1.293 \ln T + 1.821 \times 10^{-5} T$$

$$InI_3 = InI + I_2$$

$$\ln K_p = 27.082 - 23601/T + 3857/T^2 - 0.9969 \ln T + 6.087 \times 10^{-5} T$$

The thermodynamic characteristics of indium iodides were measured by several research groups.[39, 44] Tables 2 and 3 summarize the data obtained by Titov *et al.*[39] These data are consistent with the condition for the concavity of the concentration dependence of the isobaric-isothermal potential — the broken line $G(x)$.[107]

Both the yellow and red modifications of InI_3 are very hygroscopic and readily absorb water in atmospheric air. The solubility in water increases with an increase in the temperature from 92.3% at 1 °C to 95.3% at 70 °C. The density of the saturated solution at 22 °C is 3.462 g cm^{-3}, due to which it can be used to separate minerals by density. Good water solubility allows the application of indium iodide in chemical synthesis, for example:[108]

$$InI_3 + 3\,CuI + 3\,Na_2Se \longrightarrow 3\,CuInSe_2 + 6\,NaI$$

Hydroiodic acid causes salting-out of indium triiodide. The solubility decreases also in the presence of magnesium,

Table 2. Standard enthalpies of formation and absolute entropies of indium iodides.[39]

Composition	Phase	$\Delta_f H^\circ$ (298.15) /kJ mol^{-1}	S° (298.15) /J mol^{-1} K^{-1}
InI	cr	-102.5 ± 0.2	120.1 ± 0.1
InI	g	26.4 ± 0.5	268.1 ± 0.5
InI_2	crII	-176.0 ± 0.4	173.9 ± 0.4
In_2I_4	g	-215 ± 9.0	511.8 ± 8.4
InI_3	crII	-229.2 ± 0.6	205.4 ± 0.5
InI_3	crI	-224.0 ± 0.2	223.0 ± 0.4
InI_3	g	-105.4 ± 1.5	402.0 ± 2.0
In_2I_6	g	-311.9 ± 7.9	650.1 ± 8.5

Note. The following abbreviations are used: g is gas, cr is a crystal, crI is a high-temperature modification, crII is a low-temperature modification.

Table 3. Characteristics of phase transitions in indium iodides.[39]

Composition	Transition type	T/K	P/atm	ΔH°/kJ
InI	cr → l	637.5	9.08×10^{-4}	17.26 ± 0.25
InI	l → InI (g)	637.5	9.08×10^{-4}	105.12
InI_2	crII → crI	428.1	1.59×10^{-8}	1.29 ± 0.21
InI_2	crI → In_2I_4	428.1	0.59×10^{-8}	130.62
InI_2	crI → InI_3 (g) + InI (g)	428.1	1.00×10^{-8}	265.02
InI_2	crI → l	497.2	2.60×10^{-6}	11.85 ± 0.35
InI_2	2l → In_2I_4 (g)	497.2	0.90×10^{-6}	103.64
InI_2	2l → InI_3 (g) + InI (g)	497.2	1.70×10^{-6}	237.19
InI_3	crII → crI	291.5	1.27×10^{-12}	5.16 ± 0.05
InI_3	crI → InI_3 (g)	291.5	1.26×10^{-12}	118.71
InI_3	2 crI → In_2I (g)	291.5	0.01×10^{-12}	136.31
InI_3	crI → l	480.2	2.60×10^{-4}	18.48 ± 0.24
InI_3	l → InI_3 (g)	480.2	2.10×10^{-4}	95.55
InI_3	2l → In_2I_6 (g)	480.2	0.50×10^{-4}	93.13

Note. For abbreviations, see Table 2; l is liquidus.

zinc, alkali and alkaline earth metal iodides.[20] The triiodide is readily soluble in ethanol, acetone (colourless solutions) and ethyl phenyl ether (pale-yellow solution). In chloroform and carbon tetrachloride, InI_3 decomposes to form iodine, resulting in the dark-violet colour of the solution. In hexane, heptane and octane, this iodide slowly decomposes to form a white precipitate (the composition is unknown), the red modification reacting more rapidly than the yellow one. In anhydrous benzene at 25 °C, InI_3 is virtually insoluble.[24, 47]

Indium triiodide decomposes (is oxidized and hydrolyzed) to form the oxide iodide InOI upon heating in air.[80, 81] The pyrohydrolysis of InI_3 is performed also in an autoclave. The reaction of ammonia with triiodide affords a mixture of ammoniates. Ammoniates containing seven, five and two NH_3 molecules were synthesized by the reaction with liquid ammonia. At temperatures below 0 °C, the existence of ammoniates containing 20, 13 and 9 NH_3 molecules was confirmed by tensiometry.[20] The reaction of ammonia under a pressure of 0.6 – 0.8 MPa gave hexaammoniate, and its decomposition at 50, 205 and 305 °C produced penta-, tri- and monoammoniates, respectively.[109] The latter compound melts without decomposition at 130 °C and vapourizes at 450 °C. The high-temperature reaction with ammonia yields indium nitride.[110]

$$InI_3 + NH_3 \longrightarrow InN + NH_4I$$

Wu *et al.*[30] used the reaction

$$InI_3 + 3\,NaNH_2 \longrightarrow InN + 3\,NaI + 2\,NH_3$$

that was performed in benzene in an autoclave to synthesize indium nitride nanopowder.

Indium diiodide (InI_2) is a crystalline yellow compound, which readily absorbs water in atmospheric air, although it is less hygroscopic than indium triiodide. In water, this compound undergoes decomposition to form a dark-red precipitate of indium monoiodide. The decomposition in ethyl phenyl ether (phenetole) proceeds in a similar way. Indium diiodide is slowly dissolved in dilute acids in the cold, the process involving the decomposition of InI_2 and the formation of a monoiodide precipitate in the initial step. Indium diiodide is insoluble in hexane, heptane, octane and benzene.[56]

The melting point of indium diiodide is 226 °C. The polymorphism of InI_2 is an open question. The heating thermograms of this compound clearly show one more endothermic peak at 161 °C,[56] which is also observed in systems involving InI_2.[111–113] Two modifications have different densities: 4.67 g cm^{-3} for β-InI_2 and 5.25 g cm^{-3} for α-InI_2. According to the Fedorov and Akchurin,[24] the high-temperature modification has a higher density. Beck [53] solved the crystal structure of InI_2 based on single-crystal X-ray diffraction data. This compound is isostructural with $GaCl_2$ (see Table 1). The structure consists of tetrahedral $[InI_4]^-$ anions and In^+ cations, *i.e.*, this compound is monovalent indium tetraiodoindate $In^{I}In^{III}I_4$. The coordination polyhedron (CP) of In^+ can be described as an irregular eight-vertex polyhedron. Single crystals were synthesized at 180 °C, *i.e.*, in the stability region of the high-temperature modification of InI_2. Khan and Tuck obtained similar results by X-ray diffraction.[54] These data are consistent with the X-ray diffraction pattern of α-InI_2 reported by Fedorov *et al.*[56, 113] The results of Raman spectroscopy confirm the In[InI_4] structure of this modification of InI_2.[42, 114] The observed considerable jump in the density is inconsistent with the hypothesis suggested by Ichikawa and Fukushi [114] that the transition in InI_2 at 162 ± 0.5 °C is of an order – disorder type.

Gospodinov [55] determined the crystallographic characteristics of the high-density modification (see Table 1). These data are in agreement with the non-indexed X-ray diffraction pattern of InI_2 reported by Olives-Domange and co-workers.[40] It should be noted that the X-ray diffraction pattern of β-InI_2 obtained by Fedorov and co-workers [56] is not consistent with the data obtained by Gospodinov [55] and Olives-Domange *et al.*[40] Meanwhile, this pattern is identical to the characteristics of the sample investigated by Dmitriev *et al.*[50] According to the results of this study,[50] the application of elevated pressure leads to a sharp increase in the polymorphic transition temperature ($dT/dP \approx 100$°C kbar^{-1}), which rises up to 250 °C at $P = 15$ kbar. This is evidence that the density of the low-temperature modification is higher than that of the high-temperature one. Therefore, there are at least three modifications of InI_2, the interrelation between which is to be found.

At pressures > 15 kbar, the diiodide undergoes disproportionation *via* the reaction

$$2\,InI_2 = InI + InI_3$$

Diiodide InI_2 evaporates incongruently, indium triiodide being the major component in the gas phase.[39, 56] Specific conductance measurements demonstrated that melts of InI_2 and InI are ionic liquids.[56]

Solid indium monoiodide (InI) has a brown-red colour; its powder is bright-red and its melt is almost black. This compound is quite stable in air and is nonhygroscopic. It is gradually transformed into a white substance during the storage of its powder in air for a few weeks.[56] Squillante *et al.*[10] determined the nature of the reaction products (see also the study [109]): when in contact with atmospheric air, InI single crystals undergo slow degradation from the surface *via* successive oxidation and hydrolysis.

$$2\,InI + O_2 = 2\,InOI$$

$$InOI + 2\,H_2O = In(OH)_3 + HI$$

Heating of InI in air leads to its oxidation to In_2O_3. Indium monoiodide is not reduced with hydrogen even in the gas phase. The reaction with hydrogen sulfide or SO_2 gives indium sulfide. The reaction of InI with ammonia under elevated pressure affords unstable ammoniates, which decompose to form indium metal.[24, 109]

Indium monoiodide is virtually insoluble in water even upon heating. The solubility of this compound at 20 °C is 7.1×10^{-4} mol litre^{-1} (electrochemical measurements gave a similar value of 4.7×10^{-4} mol litre^{-1}). In the presence of oxygen dissolved in water, the monoiodide is gradually oxidized to indium(III) hydroxide. Meanwhile, the disproportionation of the monoiodide can also be observed (after the induction period) in experiments performed in the absence of oxygen at 60–70 °C. Halide ions, especially fluoride, activate the disproportionation.[115] Indium monoiodide is very slowly decomposed with dilute sulfuric and hydrochloric acids. The decomposition accompanied by hydrogen release proceeds somewhat faster in the presence of concentrated acids or upon heating. Indium monoiodide is decomposed with dilute nitric acid, indium metal being transferred to a solution, while iodine being precipitated as crystals. The addition of concentrated nitric acid to InI results in a vigorous exothermic reaction accompanied by extensive evolution of iodine vapour. Indium monoiodide is insoluble in saturated hydrocarbons, chloroform, carbon tetrachloride, ethanol, diethyl ether and acetone.[56]

Indium monoiodide crystallizes in the orthorhombic system (sp. gr. *Cmcm*) and is isostructural with InBr, InCl and the low-temperature modification of TlI.[57, 58] This layered structure is characterized by short cation–anion distances and is composed of zigzag cationic chains running along the *c* axis. The lone pair of the cation plays a role in the stabilization of this structure.[116] However, based on the second-harmonic generation test, Gospodinov[117] suggested the non-centrosymmetric space group $P2_12_12_1$ for InI.

According to the results reported by Ichikawa and Warren,[118] small amounts of indium are dissolved in monoiodide; the solubility increases with an increase in the temperature and reaches 1.2% at 1000 °C. The dissolution of indium in InI gives rise to colour centres (F-centres), like in alkali metal halides. The iodide is insoluble in indium metal. Indium monoiodide can be doped with a considerable amount of germanium. Wang *et al.*[119] calculated the characteristics of the solid solution $In_{1-x}Ge_xI$ ($x \leqslant 0.25$). The results of energy calculations[120] suggest that cation interstitials (Frenkel defects) are dominant intrinsic defects in InI. Bibikov *et al.*[121] reported that the interaction of defects in the InI crystal gives rise to an incommensurate phase and causes a ferroelastic phase transition at about 20 K.

Indium monoiodide is a semiconductor with a band gap of 2.0 eV.[10, 122, 123] It exhibits photoconductivity[124, 125] and photosensitivity.[23] The data on the optical properties and lattice dynamics are scarce.[122, 126–128] The layered structure of InI is responsible for strong anisotropy of its physical properties.

Initially, single crystals of InI were grown from the gas phase.[122, 126] The best results were obtained by performing the slow sublimation of InI in an evacuated quartz ampoule in a very small temperature gradient: the hot zone temperature was 300–350 °C, the condensation zone temperature was 270–300 °C. The resulting plate crystals with sizes of $2 \times 2 \times 1$ mm were suitable only for some physical studies.

Onodera *et al.*[12] used the horizontal travelling molten zone method to grow InI single crystals in a quartz ampoule filled with argon (the zone travelling speed is 5 mm h^{-1}). The Bridgman technique using evacuated quartz ampoules was applied in a number of studies[9, 11, 13, 23, 121] (the typical lowering rate is 5 mm day^{-1}).

Guliev[51] reported that the dark-red monoiodide was transformed into the orange-red modification at 150 °C and turned lemon-yellow at 210 °C. Since single crystals of dark-red InI are grown directly from a melt, these polymorphic transitions are highly improbable. No phase transitions were identified in the phase diagrams involving InI. The phase diagram for the InI–TlI system[129] is inconsistent with the conclusion drawn by Ichikawa and Fukushi[114] based on the Raman spectra. These authors suggested that InI is transformed into a CsCl-type high-temperature modification isostructural with α-TlI at a temperature higher than 208.5 °C. As Smirnov *et al.*[23] have rightly pointed, the observation of polymorphism of InI is apparently attributed to insufficient phase purity of the samples. In particular, the presence of diiodide impurity in the monoiodide gives rise to the eutectic thermal effect (see Fig. 2).

Indium monoiodide is resistant to pressure up to 8 GPa.[23] Zhang *et al.*[130] predicted the existence of a tetragonal (sp. gr. *P*4/*nmm*) high-pressure phase.

Indium monoiodide is stable in the vapour phase. At 800 K, the concentration of dimers In_2I_2 in gaseous InI is 2%.[131] The vapour pressures reported by different authors are presented in Fig. 6. High vapour pressure of indium tri- and monoiodides enables the transport of nickel *via* a chemical vapour transport reaction.[135]

The monoiodide is a promising filler for metal halide lamps due to relatively high volatility at low temperature and a low dissociation energy of the InI molecule combined with a high recombination rate[136–139] (see Section III below).

Lower indium iodides are active reducing agents. Fusing together of indium monoiodide and Cu, Hg, Ni, Fe, Co, Bi, Sb, As and Te iodides resulted in their reduction accompanied by the release of the corresponding metals.[140] The

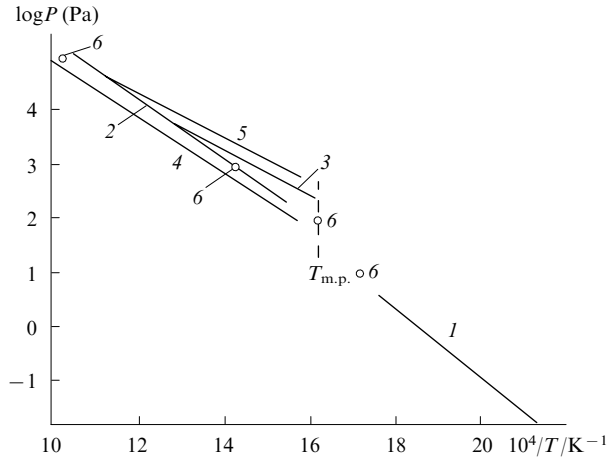


Figure 6. Temperature dependence of the vapour pressure of indium monoiodide according to different authors.
(*1*) Barrow *et al.*,[132] (*2*) Chusova;[49] (*3*) Fedorov *et al.*,[56] (*4*) Grinberg *et al.*,[133] (*5*) Sandulova *et al.*,[134] (*6*) Brewer.[96]

reduction usually begins in the solid phase (except for CuI, SbI_3 and AsI_3) at temperatures not higher than 220 °C. Indium diiodide is a milder reducing agent than InI. It reduces Cu, Sb, As, Ni and Te iodides from a melt; cobalt diiodide is resistant to indium iodide. The following equations were proposed[140] for the redox reactions that take place:

$$InI + MI = InI_2 + M \ (M = Cu, Hg)$$

$$InI_2 + 2\,MI = InI_3 + M \ (M = Cu, Hg)$$

$$3InI + BiI_3 = 3\,InI_2 + Bi$$

$$3\,InI_2 + BiI_3 = 3\,InI_3 + Bi$$

$$4\,InI + 4\,CoI_2 = InCo_2I_6 + 3\,InI_2 + 2\,Co$$

In solvents, indium monoiodide undergoes disproportionation to triiodide and the metal.[23]

Indium tri- and monoiodides are prone to form compounds with other metal iodides. The X-ray diffraction data, melting points and polymorphic transition temperatures are summarized in Table 1. Selected phase diagrams are presented in Fig. 7. It should be noted that there are serious discrepancies between the phase diagrams and the X-ray diffraction data.

According to Fedorov, Dudareva and co-workers,[86,92,143] incongruently melting hexaiodoindates M_3InI_6 are formed in $MI-InI_3$ systems (M = Na, K, Rb, Cs). However, the X-ray diffraction studies attested[59,60] to the formation of tetraiodoindates $MInI_4$ in these systems (see Table 1). Single crystals were synthesized by slow cooling of melts. All of the structures contain nearly regular tetrahedra $[InI_4]^-$. The coordination number of alkali metal cations varies from 6 (Li, Na) to 9 (Rb), 11 (Cs) and 12 (K). Taylor and Kloo[42] measured Raman spectra and revealed the formation of tetrahedral $[InI_4]^-$ ions in $MInI_4$ complexes (M = K, Cs), which were prepared by fusing together a mixture of iodides at 200–250 °C. According to this study, $KInI_4$ is the only compound in the $KI-InI_3$ system, whereas the $CsI-InI_3$ system contains also the compound $CsIn_2I_7$ with the $[In_2I_7]^-$ anion. These anions are vertex-sharing double tetrahedra, which are known also for compounds with gallium chloride.[26] The formation of the $CsInI_4$ complex was observed also in the reaction of InI_2 with CsI.[111]

The compound $TlInI_4$ was found by studying the phase diagram for the $TlI-InI_3$ system,[92,94] while Olives-Domange and co-workers[40] demonstrated that the compound $AgInI_4$ was missed in the relevant study.[92] The compounds $CuInI_4$ and Cu_3InI_6 are marked in the phase diagram for the $CuI-InI_3$ system;[89] however, the structural data are lacking.

The tetrahedral $[InI_4]^-$ anion is the main structural unit of iodoindate(III) complexes. This anion was found in the crystal structure of NH_4InI_4,[61] as well as in such unusual compounds as $(NH_4)_2[(AuI_4)(InI_4)]$ and $(Bi_8)_3Bi[InI_4]_9$ (see Table 1). The latter compound contains the cluster cations Bi_8^{2+}. The $[InI_4]^-$ anion is the structural unit of the compound $TeI_4 \cdot InI_3$, which contains also trigonal-pyramidal TeI_3^+ cations,[63] *i.e.*, the formula of this compound should be written as $[TeI_3][InI_4]$. According to Fedorov *et al.*,[64] this congruently melting compound is metastable and disappears after annealing at 120 °C for 600 h. As can be seen in the phase diagram (see Fig. 7, *f*), the compounds Te_2InI_{11} and Te_3InI_{15} were produced after 1000 h annealing.

The synthesis of compounds in iodide systems with InI_3 in the absence of a solvent normally takes a very long period of time (a few months).[24,142] In a system with manganese diiodide, only the compound $MnIn_3I_{11}$ is stable and decomposes below the eutectic temperature (see Fig. 7 *d*). Two other compounds ($2\,InI_3 \cdot 3\,MnI_2$ and $InI_3 \cdot 3\,MnI_2$) are metastable. They were observed in the case of an insufficient annealing time (shorter than 500 h). In a system with iron(II) iodide, the stable compound Fe_4InI_{11} is formed below the eutectic temperature (see Fig. 7 *a*), while the compounds MIn_2I_8 (M = Co, Ni), which were found in systems with cobalt and nickel iodides (see Fig. 7 *b*,*c*), are metastable and disappear after annealing. The compound $CdIn_6I_{20}$, which was found in the first study,[88] undergoes a polymorphic transition at 298 °C (see Fig. 7 *g*) and is evidently metastable. In equilibrium state, the system contains cadmium tetraiodoindate $Cd(InI_4)_2$ with a congruent melting temperature of 195 °C, and this compound was also found in the melt (see Fig. 7 *h*).[143]

The precipitation from aqueous solutions gives numerous hydrated binary compounds of indium iodide with other metal iodides. For example, the compound $MgI_2 \cdot InI_3 \cdot 6\,H_2O$ (1 : 1 : 6), as well as hydrates with component ratios $MgI_2 : InI_3 : H_2O = 1 : 2 : 11$ and 3 : 4 : 26, are formed with magnesium iodide; compounds with component ratios $CaI_2 : InI_3 : H_2O = 1 : 1 : 6$; 1 : 1 : 8 and 2 : 3 : 12 with calcium iodide; compounds with component ratios $SrI_2 : InI_3 : H_2O = 1 : 1 : 10$ and 2 : 1 : 18 with strontium iodide; compounds with component ratios $BaI_2 : InI_3 : H_2O = 1 : 1 : 5$ and 1 : 2 : 10 with barium iodide; compounds with component ratios $ZnI_2 : InI_3 : H_2O =$ 2 : 3 : 13 and 1 : 1 : 5 with zinc iodide; the compound $TlI \cdot 2\,InI_3 \cdot 3\,H_2O$ with thallium iodide.[20]

Indium triiodide forms eutectic-type systems with zinc iodide[93] (with limited solid solutions), arsenic,[144] antimony,[145] bismuth[91] triiodides and silicon, germanium,[144] tin[64] tetraiodides (see Fig. 7 *e*).

A system with aluminium iodide is characterized by solid solutions based on the components and the formation of two incongruently melting berthollide phases (see Fig. 4 *b*). One of these phases forms an ordered superstructure corresponding to the composition $2\,InI_3 \cdot AlI_3$.[84] Continuous solid solutions with a minimum in the liquidus are present in the GaI_3-InI_3 system.[146] These results are in agreement with the data on the isostructurality of gallium and indium triiodides.[84]

Indium triiodide forms compounds with a much broader range of metal halides compared to the trichloride and tribromide.[24] However, many of these compounds are metastable. It should be noted that many iodide compounds have compositions that were not found for chlorides or bromides. The formation of heterovalent solid solutions typical of indium trichloride[147,148] is weakly pronounced for the triiodide. The highest solubility in indium(III) iodide is observed in the system with zinc iodide (10 mol.%), whereas solid solutions are absent in systems with cobalt and nickel iodides, although it is the cobalt and nickel chlorides that have the highest solubility in indium(III) chloride.

In the binary systems involving indium monoiodide and another metal iodide [except for alkali metals and thallium(I)], compounds similar in composition to thallium

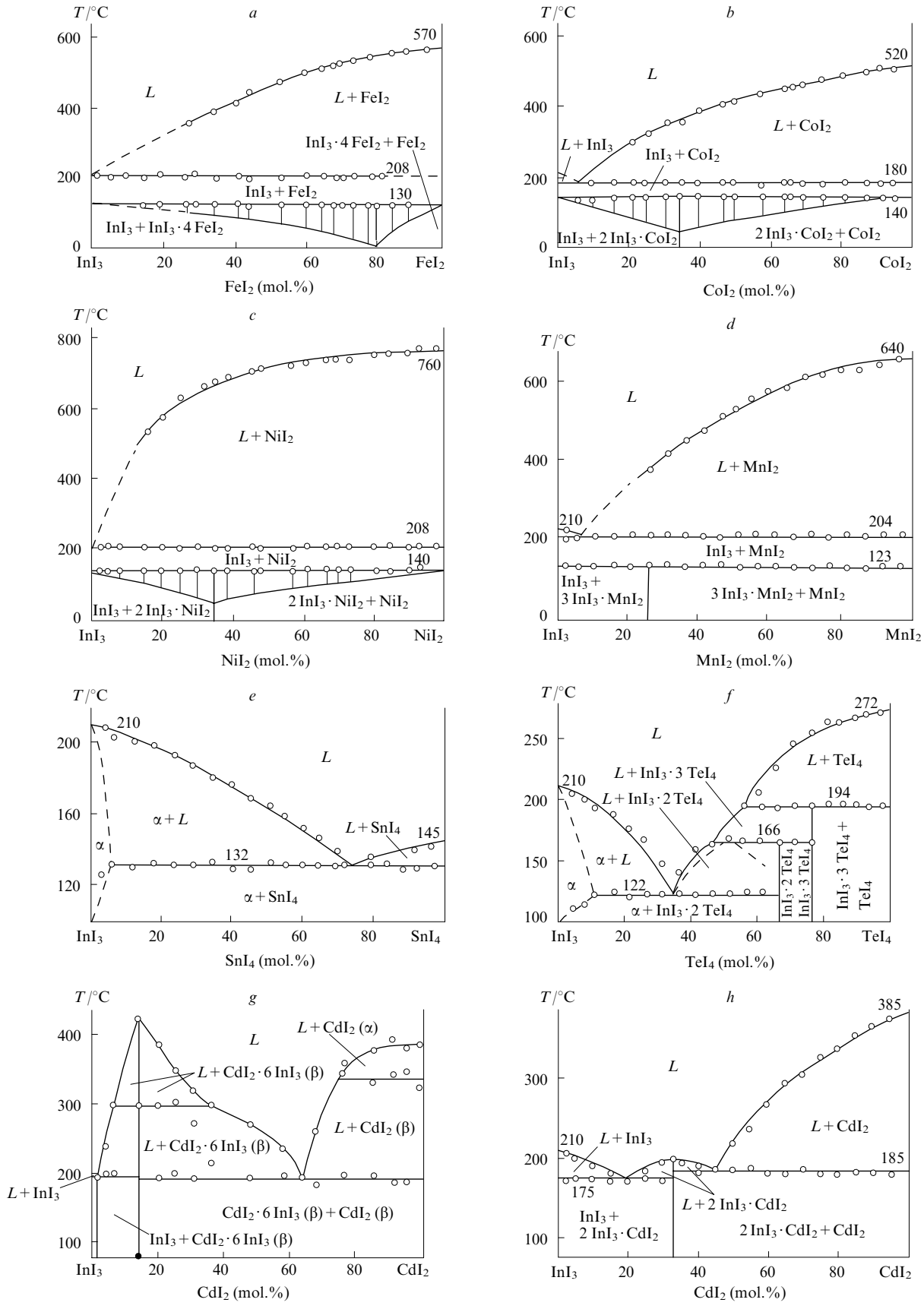


Figure 7. Phase diagrams for systems of InI_3 with FeI_2 (*a*),[141] CoI_2 (*b*),[141] NiI_2 (*c*),[141] MnI_2 (*d*),[64] SnI_4 (*e*),[64] TeI_4 (*f*),[64] CdI_2 (*g*),[88] CdI_2 (*h*).[142]
In Figs *e* and *f*, α is a solid solution based on the high-temperature modification α-InI_3.

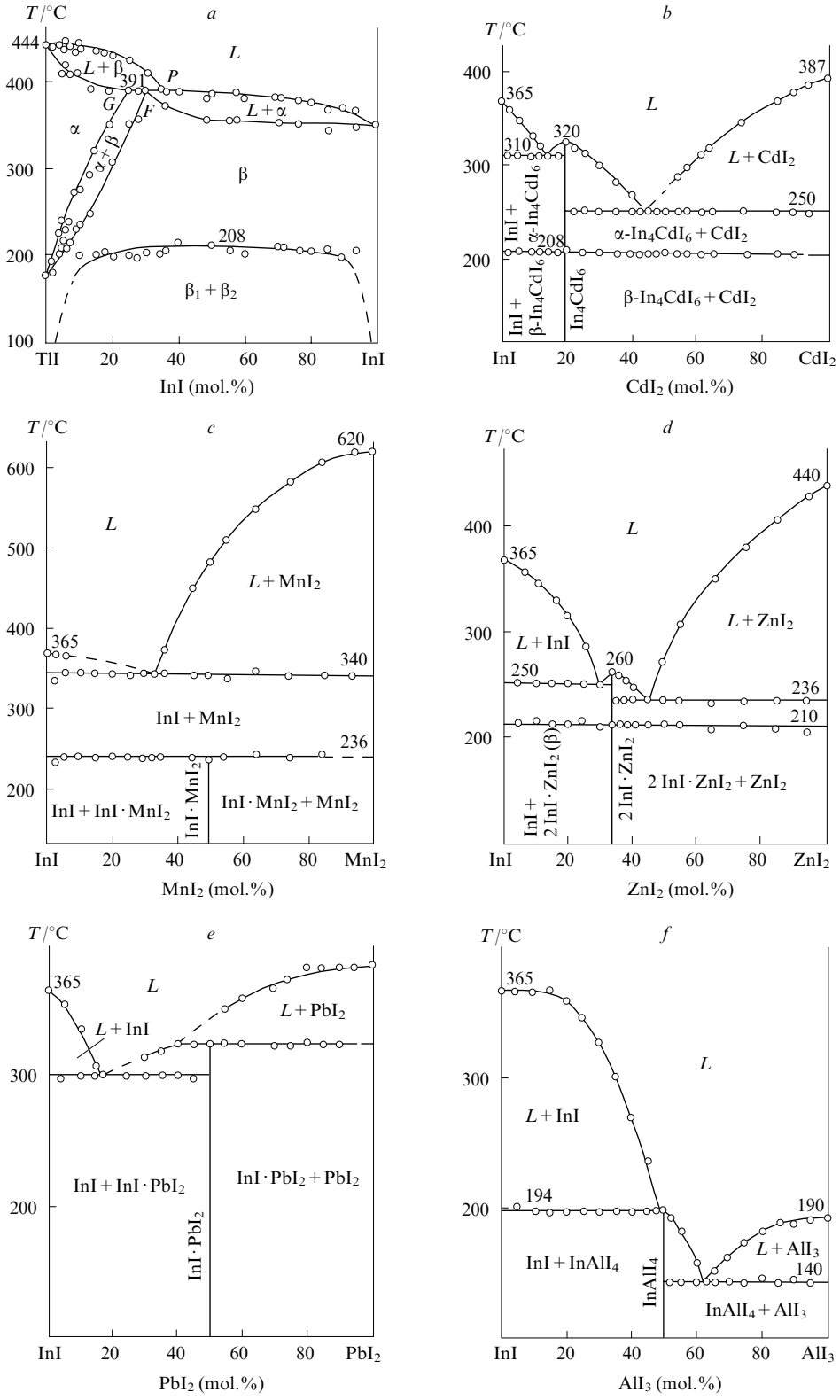


Figure 8. Phase diagrams for InI systems with TlI (*a*),[129] CdI_2 (*b*),[71] MnI_2 (*c*),[79] ZnI_2 (*d*),[79] PbI_2 (*e*),[79] AlI_3 (*f*).[79] In Fig. *a*, β is a continuous solid solution, which decomposes into two limited solid solutions (β_1 and β_2).

compounds are produced. Examples of phase diagrams for such systems are shown in Figs 8 and 9.

The results obtained by Olives-Domange *et al.*[40] in the repeated study of the AgI – InI system are similar to those reported by Fedorov *et al.*[79] Thus, two compounds having incongruent melting behaviour were found (see Fig. 9 *a*). Gospodinov[69] amended the space group of the crystal structure of $AgIn_2I_3$ to the non-centrosymmetric space

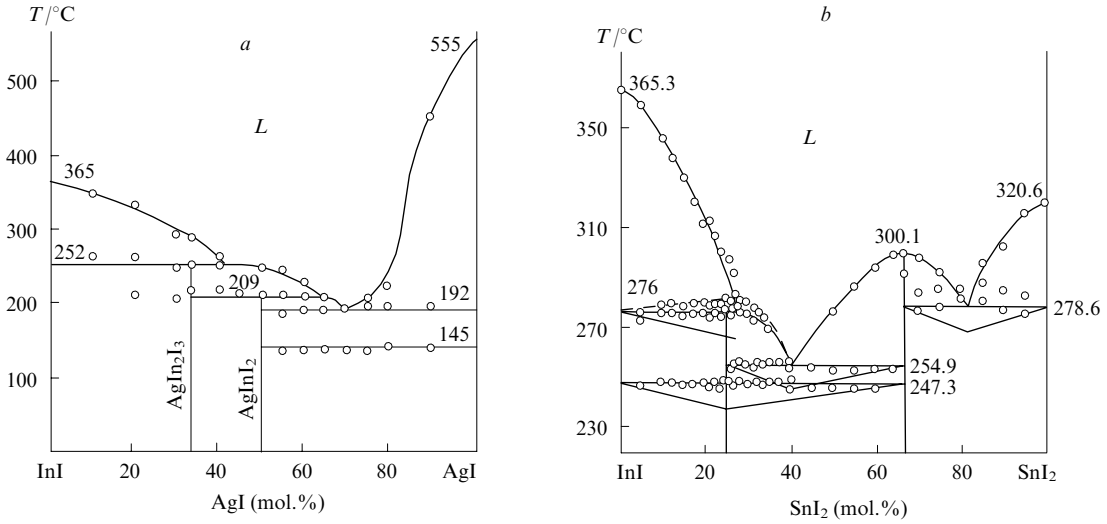


Figure 9. Phase diagrams for the InI – AgI (*a*)[40] and InI – SnI_2 (*b*)[75] systems.

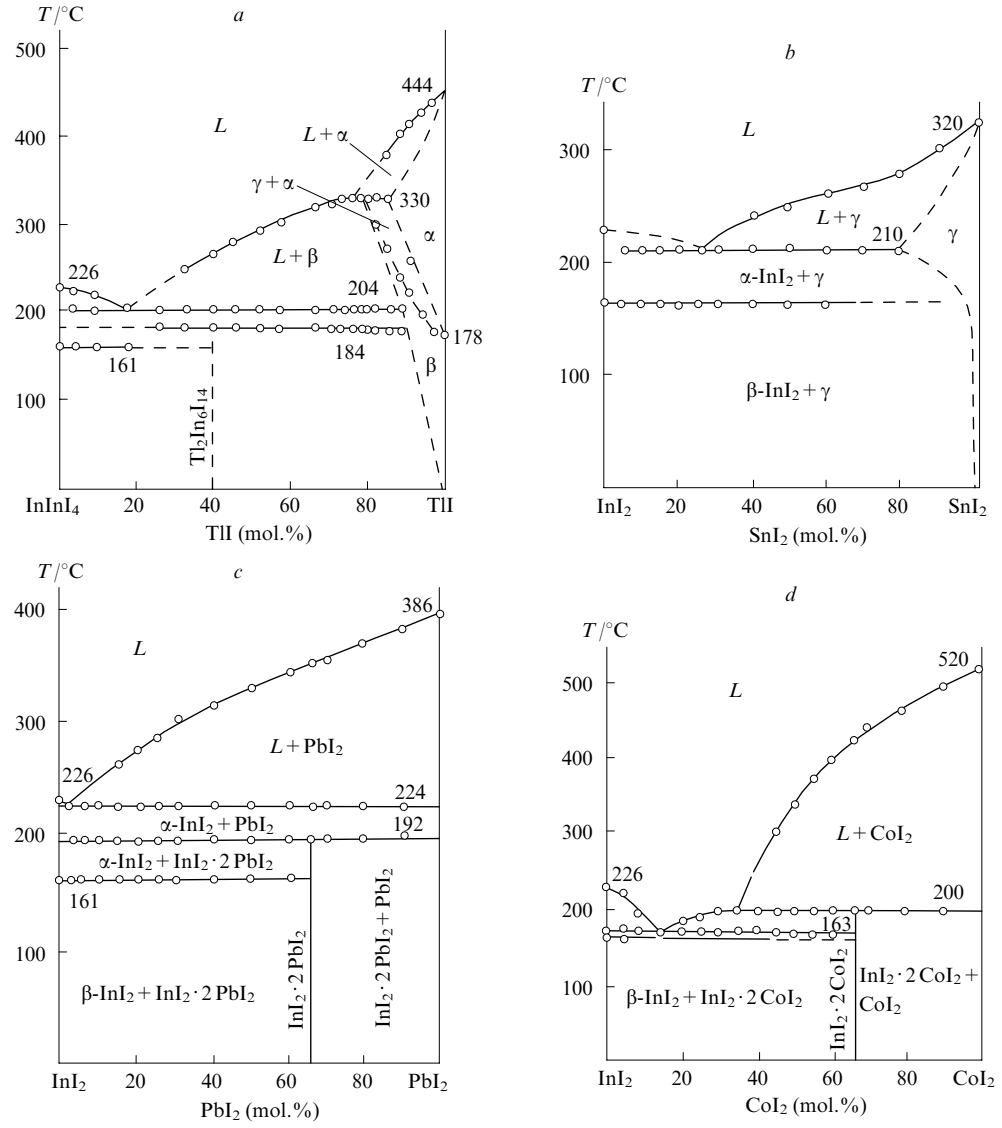


Figure 10. Phase diagrams for InI_2 systems with TlI (*a*),[113] SnI_2 (*b*), PbI_2 (*c*), CoI_2 (*d*).[112] In Fig. *a*, α and β are solid solutions based on the low-temperature modifications of TlI; in Fig. *b*, γ is a solid solution based on SnI_2.

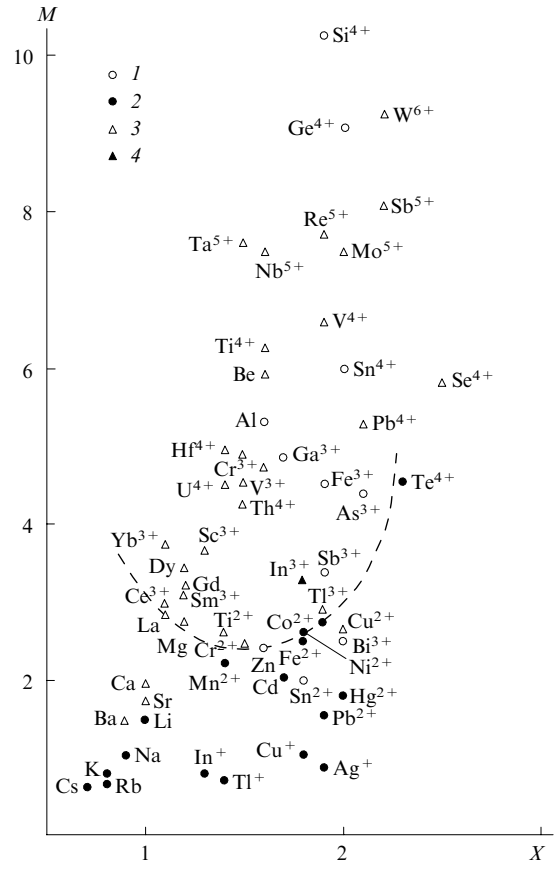


Figure 11. Diagram of the cation generalized moment (M) *versus* the electronegativity (X) for a group of InI_3-MI_n systems.
(*1*) The corresponding iodide does not form compounds with InI_3, (*2*) the corresponding iodide forms compounds with InI_3 (*3*) the system has yet to be studied (*4*) the basic compound.

group $R3m$ based on the results of the second-harmonic generation measurements. The X-ray diffraction pattern of the compound $InAlI_4$, which was synthesized by Fedorov *et al.*[79] in the study of the phase diagram (see Fig. 8 *f*), is in agreement with the X-ray diffraction data reported by Timofte and Mudring.[78] The revision was made for the $InI-SnI_2$ system. The congruent melting behaviour and the absence of polymorphic transitions in $InSn_2I_5$, which were reported by Denisov*et al.*,[71] were confirmed by Stöwe and Beck.[75] However, the composition of the incongruently melting compound was corrected in the latter investigation, where it was reported that In_3SnI_5 rather than In_4SnI_6 is generated (see Fig. 9 *b*). The discrepancy was observed for the $InI-PbI_2$ system. Thus, instead of the compound $InPb_2I_5$ synthesized by Beck *et al.*,[77] the compound $InPbI_3$ was found in the phase diagram (see Fig. 8 *e*),[79] the X-ray diffraction pattern of the latter compound being inconsistent with the results published for the compound $InPb_2I_5$ in the study.[77] It is unclear which of the two polymorphic modifications of In_4CdI_6 (see Fig. 8 *b*) correspons to the structural data obtained by Beck and Milius[70] (see Table 1). Apart from the compounds found in the phase diagrams for the $InI-MI_n$ systems, a series of binary iodides were synthesized; for example In_4TiI_6 (see Table 1). Meanwhile, some compounds and their polymorphs that are present in the phase diagrams have yet to be structurally characterized. Most of these compounds undergo incongruent melting and/or polymorphic transitions, which interfere with the preparation of their single crystals from melts.

Compounds with indium diiodide were found in systems with TlI,[113] PbI_2, CoI_2 (Ref. 112) (Fig. 10). The structural data from these compounds are lacking.

Trivalent indium forms oxo and chalcogenide iodides of type InXI (X = O, S, Se, Te) (see Table 1).[80–83] In the In–Te–I system, apart from InTeI, the compound In_3Te_3I was synthesized by the direct synthesis from the elements.[149,150] Selenide iodide InSeI can be synthesized by the reaction of In_2Se_3 with gaseous iodine.[151]

In order to integrate data on phase equilibria and the formation of compounds in systems with indium tri- and monoiodide, we present the diagrams of the generalized moment (M) of the cation (charge-to-ionic radius ratio of the cation) *versus* the electronegativity (X) for groups of the InI_3-MI_n and $InI-MI_n$ binary systems (see Figs 11 and 12, respectively). These diagrams have compound formation regions. The boundaries of the regions, where the formation

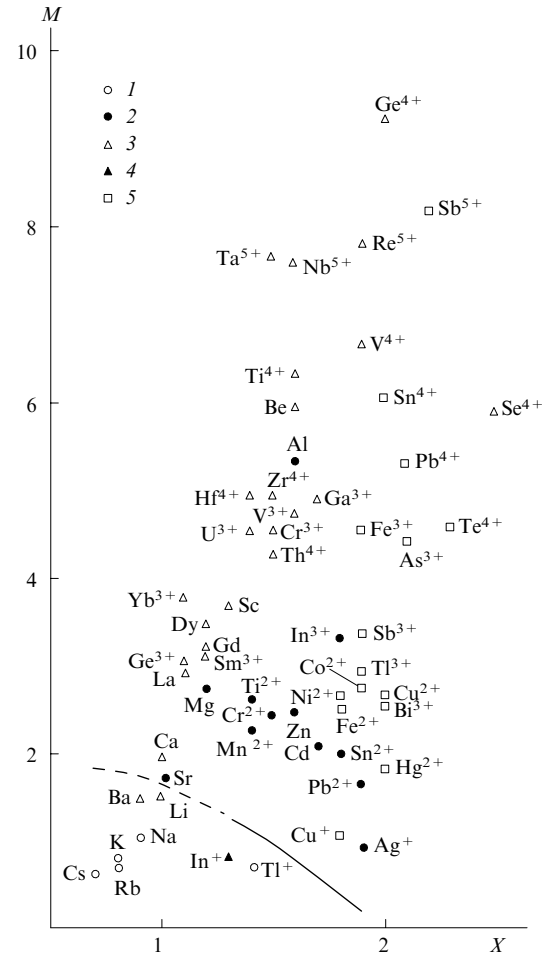


Figure 12. Diagram of the cation generalized moment (M) *versus* the electronegativity (X) for a group of $InI-MI_n$ systems.
(*1*) The corresponding iodide does not form compounds with InI, (*2*) the corresponding iodide forms compounds with InI, (*3*) the system has yet to be studied, (*4*) the basic compound, (*5*) the reduction reaction takes place.

of compounds takes places, are marked with lines (the dashed line indicates that the position of this boundary is not quite definite). This approach was suggested by Fedorov [152] and was then successfully applied to analyze the complexation in groups of chloride and fluoride systems,[152–154] including InF_3-MF_n.[155]

For a group of InI_3-MI_3 systems, the separation of the complexation region (the shape of the boundary curve resembles that for the group of $InCl_3-MCl_n$ systems [153]) is not distinct. Apparently, this is due to the difficulties in the synthesis of compounds and the formation of a large number of metastable phases. It is necessary to check whether there are no compounds in systems with SnI_2 and BiI_3 and to study the reactions of InI_3 with Zr and Hf tetraiodides and As, Sb and Bi pentaiodides. Compounds with alkaline earth metal iodides would be expected to be formed. According to the structural data, all of the compounds that are formed are tetraiodoindates.

The situation is simpler for a group of $InI-MI_n$ compounds. In this case, diverse compounds are produced, in which the monovalent indium cation has a passive role (outer-sphere cation). The $M-X$ diagram (see Fig. 12) is similar to that for the group of $TlCl-MCl_n$ systems.[153] A large number of new indium monoiodide compounds, including those with rare-earth metal, beryllium, calcium, gallium, zirconium and hafnium iodides, would be expected to be formed.

The available data on inorganic compounds of indium iodides are largely controversial. The polymorphism of indium mono- and diiodides remains an open question. The factors responsible for discrepancies between the published phases diagrams, the results of synthetic studies and structural data remain to be disclosed. Many compounds that were synthesized have yet to be structurally characterized. A large number of new compounds, especially with indium monoiodide, would be expected to be synthesized.

III. Use of indium iodides in metal halide lamps

In modern industry, indium iodides are used as light-emitting additives in metal halide gas-discharge lamps. Readily vapourizable and ionizable halides (*e.g.*, aluminium, thallium, tin and/or bismuth halides [156]) are added in order to produce radiation within a preselected region of the spectrum or create visible light by combining radiation in different regions of the spectrum. The first lamps containing indium iodides were invented in the 1960s.[157, 158] Indium iodides have advantages over indium metal due to their high volatility (see Section II); however, they can react with the glass thus shortening lamp life. This problem (common to many other lamps) was quite easily solved by using quartz instead of usual silica glasses. Quartz glass devitrifies in a narrow temperature range (from 900 to 1000 °C) and can withstand considerable pressure. Therefore, quartz iodide lamps can safely operate at lower or higher temperatures [158] and at a pressure from vacuum to atmosphere or to high pressure. Due to these facts, almost all of indium iodide lamps were made of quartz glass (in some lamps, modern transmitting ceramic materials, such as Al_2O_3 or $Y_3Al_5O_{12}$, are used [159, 160]). Moreover, quartz proved to be very useful in generating UV light.[161] However, there are some disadvantages and shortcomings related to the use of quartz in metal halide lamps.

1. Some halides (*e.g.*, rare-earth iodides) react with quartz to form oxoiodides together with SiI_4.[162] A similar transformation of oxide to iodide occurs in the reaction with alumina at high temperatures [162] (*i.e.*, both these materials have lifetime limitations when used in manufacturing technology of metal halide lamps).

2. Because of the relatively high (several hundred degrees Centigrade) [158, 163–165] operating temperature of the lamp, its quartz surface should not be touched with bare hands or should not be contaminated with foreign organic substances, since hot spots on the lamp surface immediately undergo charring to form carbon that reacts with the quartz surface, resulting in the reduction of the latter and cracking. For instance, Jack and Koedam [166] recorded the temperature of 260 °C on the surface of a 400 W lamp, while the temperature of the lamp walls from the inside was 1000 K, and the arc temperature was 4000–7000 K with an effective colour temperature of 4500 K.

3. Quartz used in metal halide lamps should be of high purity; otherwise iodides, which are usually inert to SiO_2, can react with silica. Thus, Reiling [167] found that NaI does nor react with quartz glass at 300–1500 K only in the absence of contamination.

Indium iodide lamps were invented almost simultaneously in the USA and Europe by General Electric,[158, 168, 169] Westinghouse Electric Company [170, 171] and Paris Lamp Company.[156] Lamps emitting visible light (Fig. 13) were constructed by introducing a mixture of NaI (yellow component), TlI (green component) and InI (blue component;

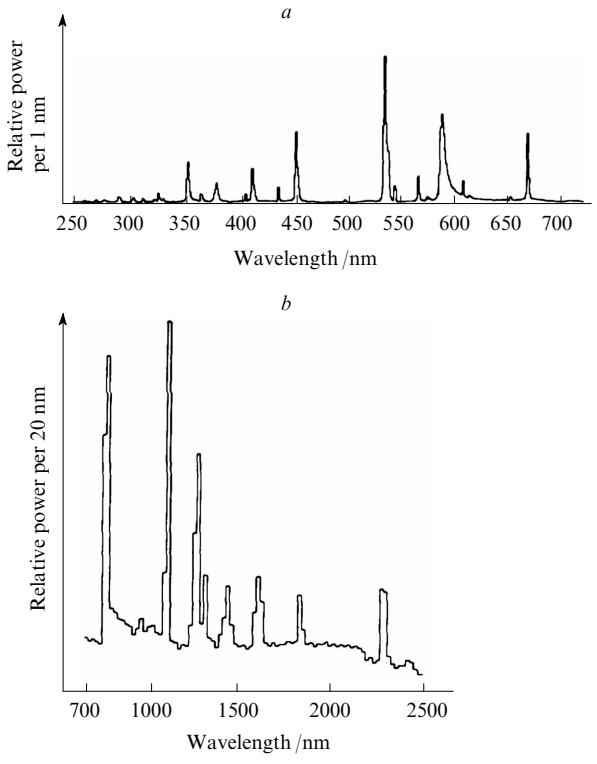


Figure 13. Spectral power distribution from visible light-emitting gas-discharge lamps containing Na, Tl and In iodides.[166]
(*a*) UV and visible part, (*b*) IR part.

emission lines at 451.1, 410.2, 325.8 and 325.6 nm and a band at 250–300 nm [172–174]) and by filling the bulb with an argon–mercury mixture.[166, 168, 170, 171] The latter two components are necessary in order to maintain the arc discharge and evaporate iodides during the operation of the lamp. However, it was found that the emission spectrum of the Hg–Ar–NaI–TlI–InI lamp is temperature-dependent and, consequently, changes during the heating of the lamp.[167] Indium and thallium monoiodides are preferred over the corresponding triiodides because they operate with lower starting voltage [175] and emit more light.[167] In the patent,[156] it was reported that the Hg–Ar–NaI–TlI–InI lamp generates a total power flow of 15, 97 and 98 W in the UV, visible and IR regions, respectively, for a rated power of 400 W. It was also found that there is a linear correlation $W_1 = 0.65W - 52$ W between the discharge power (light emission output) W_1 and the input electric power W. Such high power output allows the use of metal halide lamps as heaters.[156–175]

Due to lower ionization potentials of sodium (2.1 eV), thallium (2.4 eV) and indium (3.0 eV) compared to that of mercury (4.5 eV), mercury ions can easily ionize Na, Tl and In atoms in a steady-state electric discharge in argon gas. The Hg–Ar–NaI–TlI–InI composition for metal halide lamps emitting visible light remained virtually unchanged up to the 1970s, when researchers began to extend the range of the added iodides, including particularly rare-earth iodides and using the following chemical compositions of the discharge medium of the lamps: Hg–Ar–LuI_3–InI–CsI,[176] Hg–Ar–CeI_3–NaI–SmI_2–CsI–InI,[177] Hg–Ar–NaI–CaI_2–DyI_3–NdI_3–Cd–Tl–In,[178] Hg–Ar–NaI–TlI–CeI_3–InI,[179] Hg–Ar–NaI–ScI_3–TlI–InI–NaBr.[180] Scandium, yttrium, lanthanum, gadolinium and holmium provide high emission intensity in the blue part of the visible region of the spectrum (holmium makes also a contribution to the red part of the spectrum) and can be a good replacement for indium, particularly taking into account that rare-earth dopants produce higher light output compared to indium.[177, 178]

Since the 1980s, there has been a significant increase in the number of patent applications for indium iodide lamps with a lower power output (from ~300–400 to ~100 W or less). This may be due to the wider use of these lamps in the household and automotive industry. In automotive lamps, argon is sometimes replaced with xenon.[181–184] Although lamps based on argon and indium iodide have a longer lifetime, are easily ignited and are characterized by higher luminous efficacy compared to xenon lamps,[167] the latter are preferred from an energy efficiency standpoint.[183] Besides, xenon high-intensity discharge (HID) automotive headlamps produce a more suitable spectral range of the emitted white light (colour rendering).[185]

In the late 20th century–beginning of the 21st century, the further development of indium iodide lamps, as part of the overall technological upgrading and innovation of metal halide lamps, resulted in the invention of mercury-free lamps [186–192] and electodeless devices,[193–196] in which light emission of the discharge medium of the lamp is generated by microwave radiation. The removal of the mercury metal component is in compliance with environmental regulations, while the electrodeless modification of microwave gas-discharge lamps increases the efficiency of the lamp (decrease in heat loss *via* heat transfer by metallic electrodes) and the lifetime (prevention of corrosion of electrodes by halide vapour). The compositions of iodide mixtures used in the discharge medium of lamps were further extended:

the 1980s: Hg–Ar–TlI–InI–CdI_2;[197]

the 1990s: Hg–Xe–InI–ZnI_2–LiI–TlI,[198] Hg–Xe–NaI–ScI_3–TlI–InI–SnI_2–DyI_3–HoI_3–TmI_3–ThI_4–CdI_2–CsI,[181, 184] Hg–Ar–ZnI_2–InI–TlI–LiI–LaI_3–ScI_3–DyI_3;[183]

the 2000s: Hg–Ar–AlI_3–InI–ThI_4,[195] Xe–NaI–ScI_3–ZnI_2–InI;[199]

the 2010s: Hg–Ar–LiI–GaI_3–AlI_3–InI_3–ZnI_2–SnI_2,[200] Hg–Ar–NaI–TlI–CeI_3–InI–CaI_2,[201] Xe–NaI–ScI_3–InI_3–ZnI_2–TmI_3–MnI_2,[202] Xe–Ar–NaI–dScI_3–TmI_3–InI–ThI_4.[203]

The theoretical modelling of mercury-free Ar–InI plasma was performed by Ögün, Kaiser and co-workers [204, 205] in relation to their application in gas-discharge lamps.

It should be emphasized that, despite the well-known ability of different metal iodides to form complexes with alkali metal halides, including in the gas phase, and, correspondingly, to affect the concentration of light-emitting components in the active medium of gas-discharge lamps (see, for example, Ref. 162), this issue has not yet been considered in relation to indium iodides. Meanwhile, since rare-earth iodides can apparently form complexes with indium monoiodide, which is evidenced by the analysis of the diagram of the cumulative moment *versus* electronegativity (see Fig. 12), it is of interest to isolate such complexes and study their vapour pressure and thermal stability. The same applies to known binary iodides, such as $NaInI_4$ and $InAlI_4$ (see Section II and Table 1).

Patents on metal halide lamps are summarized in Table 2 in the electronic supplementary information (see iopscience.iop.org/journal/0036-021X).

IV. Complex compounds of indium iodides

IV.1. Indium(III) complexes

As demonstrated in Section II, all inorganic compounds of indium triiodide with other metal iodides, the structures of which were determined, are tetraiodoindate complexes containing the tetrahedral $[InI_4]^-$ anion. Vibrational spectroscopic study of the compound $CsIn_2I_7$ demonstrated that it contains the $[In_2I_7]^-$ anion composed of two $[InI_4]^-$ tetrahedra linked by a bridging iodine atom.

Complexes of InI_3 with organic ligands are highly diverse. Compounds of InI_3 with propylamine,[206] phenanthroline $[In(phen)_3I_3]$ [207] and pyridine (Py) [208] were among the first that were described in the 1940–1950s. Later on, Fairbrother *et al.*[209, 210] reported the results of investigation of the vapour pressure and other thermodynamic characteristics of indium complexes soluble in diethyl ether: $InI_3 \cdot 2\,Me_2O$, $InI_3 \cdot Et_2O$, $InI_3 \cdot 2\,THF$, $InI_3 \cdot Pr^i_2O$, $InI_3 \cdot 2\,Pr^i_2O$, $InI_3 \cdot Bu^n_2O$, $InI_3 \cdot 2\,Bu^n_2O$, $InI_3 \cdot 4$ dioxane [209] and $InI_3 \cdot 2\,Me_2S$, $InI_3 \cdot 3\,Me_2S$, $InI_3 \cdot Et_2S$, $InI_3 \cdot 2\,Et_2S$, $InI_3 \cdot 3\,Et_2S$, $InI_3 \cdot 2\,THF$.[210] Carty *et al.*[211, 212] published the vibrational spectra, data on thermal stability and melting points of indium(III) complexes with various organic ligands: $InI_3(DMSO)_2$, InI_3Py_3, $InI_3(Ph_3PO)_2$, $InI_3(Ph_3P)_2$, $InI_3(bipy)_{1.5}$ (bipy is 2,2-bipyridine) and $InI_3(DMAA)_{1.5}$ (DMAA is dimethylacetamide) (spectra, thermal stability),[211] $InI_3 \cdot 2\,PMe_3$, $InI_3 \cdot 2\,PPhMe_2$, $InI_3 \cdot 2\,PEt_3$ and $InI_3 \cdot PCy_3$ (Cy is cyclohexyl) (spectra,

melting points, molecular mass measurements in solution).[212] Gynane *et al.*[32] confirmed the results obtained by Fairbrother *et al.*[209] concerning the adduct $InI_3 \cdot Et_2O$ mentioned above. In addition to the study performed by Carty *et al.*,[211] who characterized the pyridine complex of indium triiodide, Ivanov-Emin *et al.*[213] investigated, a few years later, the phase diagram for the InI_3–α-aminopyridine system (α-NH_2-Py) and detected the compounds $2\,InI_3 \cdot$ α-NH_2-Py and $InI_3 \cdot 2$(α-NH_2-Py) having congruent melting behaviour at 207 and 116 °C, respectively. In the beginning of the 1970s, Contreras and Tuck[214] investigated in detail the properties of cyclopentadienyl (Cp) iodine derivatives of indium and characterized such compounds as $CpInI_2$, $CpInI_2$(bipy), $CpInI_2$(phen), Cp_2InI and $[NPr^n_4]^+[CpInI_3]^-$.

It should be noted that the authors of the above-mentioned earlier publications[32,206–214] devoted to complexes of indium(III) iodide with organic ligands did not employ X-ray powder diffraction or other diffraction methods in order to study the crystal structures of the synthesized compounds and/or describe their phase characteristics.

More recent studies demonstrated that indium(III) complexes with organic ligands are highly diverse. This diversity significantly complicates the generalization and hinders the concise classification of the properties and structures of indium(III) complexes. Therefore, the knowledge is limited to traditional descriptive chemistry.

For example, the crystal structure determination of $InI_3(DMSO)_2$ demonstrated that this complex is the cationic compound $[InI_2(DMSO)_4]^+[InI_4]^-$ with *cis*-cations $[I_2In(DMSO)_4]^+$ in the crystal lattice.[215]

As opposed to the preliminary characterized complexes of In^{III} iodide with different organic ligands, the dithiolate complex $InI(CF_3CS)_2$ with the five-membered InC_2S_2 ring was synthesized by the insertion of indium monoiodide into 1,2-bis(trifluoromethyl)dithiethene (heating under reflux in chloroform in the presence of catalytic amounts of ethanol for 12 h).[216] This reaction is, to some extent, similar to the redox insertion of InI into dichalcogenide bonds in the reactions of InI with the corresponding organic reactants (see Section V). The compound $InI(CF_3CS)_2$ reacts with such organic ligands as DMSO, bipyridine and 1,10-phenanthroline to form the complexes $InI(CF_3CS)_2 \cdot 4$ DMSO, $InI(CF_3CS)_2 \cdot 1.5$ bipy and $InI(CF_3CS)_2 \cdot 1.5$ phen, respectively.[216]

A similar insertion was observed by de Souza *et al.*,[217] who obtained crystals of $CH_2(tmtu)_2(InI_4)_2$ by stirring 1 equiv. of InI with 6 equiv. of pure CH_2I_2 for 4 h followed by the treatment of the mixture with 2 equiv. of 1,1,3,3-tetramethyl-2-thiourea (tmtu) (room temperature, 12 h, 69% yield). A similar reaction with the bromide produces $Br_3InCH_2SC(NMe_2)_2$, whereas the iodide forms a compound composed of isolated $[InI_4]^-$ tetrahedra and $[CH_2\{SC(NMe_2)_2\}_2]^{2+}$ cations.[217]

Most indium(III) iodide complexes contain four-coordinate $[InI_4]^-$-like In units. In particular, the *N*,*N*′-dimethyl-4,4′-bipyridinium complex salt $(Me_2bipy)In^{III}I_5$, which was prepared by the reaction of triiodide InI_3 with *N*,*N*′-dimethyl-4,4′-bipyridinium iodide in methanol, contains $[InI_4]^-$ and I^- anions.[218] As opposed to the $[InCl_5]^{2-}$ complexes, related $[InI_5]^{2-}$ anions are not formed due apparently to the larger size of I^- anions compared to Cl^-.

The reaction of equimolar amounts of InI and benzoyl peroxide in dichloromethane at −20 °C in the presence of excess pyridine affords the complexes $InI(OBz)_2 \cdot 2$ Py[209] containing an indium atom inserted into the O–O bond (for comparison, see below the insertion of indium into the dichalcogenide bond considered in Section V). Peppe and Tuck[219] reported the data on the complexes $InI(SeMe)_2 \cdot 2$ Py, $InI(SPh)_2 \cdot NPr^n_4I$, $InI[Co(CO)_4]_2 \cdot 2$ Py, which are generated *via* the insertion of indium monoiodide into Se–Se, S–S and Co–Co bonds, like the formation of $InI(SMe)_2$ Py from MeSSMe. However, the reactions with n-butyl disulfide and/or *tert*-butyl disulfide lead only to the reduction of In^I to the metal. Indium monoiodide reacts with $(CO)_3Co(\mu\text{-}CO)_2Co(CO)_3$ in a mixture of pyridine and dichloromethane accompanied by the cleavage of the bridging bonds of CO groups and the formation of $InI[Co(CO)_4]_2 \cdot 2$ Py. The complexes $Mn_2(CO)_{10}$ and $[(\eta^5\text{-}Cp)Fe(CO)_2]_2$ are not involved in similar reactions with InI.[219]

The dropwise addition of a solution of 2 equiv. of MeLi in diethyl ether to an ethereal solution of InI_3 at −78 °C followed by the addition of *tert*-butylamine at room temperature gives the complex $Me_2InI \cdot Bu^tNH_2$.[220] The crystal structure of this complex contains $Me_2(I)In\cdots NH_2Bu^t$ structural units, in which the indium atom is surrounded by two methyl carbon atoms, one iodide ion and the nitrogen atom of Bu^tNH_2 (single-crystal X-ray diffraction data).

On the contrary, the coordination environment of the indium atoms (both In^I and In^{III}) in the complexes $\{HB(3,5\text{-}Me_2\text{-}pz)_3\}_2InI$ and $[\{MeGa(pz)_3\}_2In]^+[InI_4]^-$ (pz is pyrazol-1-yl) can be described as a distorted octahedron formed by six pyrazole nitrogen atoms of two tridentate ligands.[221] This structure correlates with the six-coordinate central indium atom in *trans*-$[I_2In\{OP(NMe_2)_3\}_4]^+I^-$ (Ref. 222).

Complexes of In^{III} iodides can be synthesized directly from the metal by the simultaneous oxidation and complexation, in particular, using stoichiometric amounts of R_3PI_2 in diethyl ether at room temperature under nitrogen over 7 days.[223]

$$3\,Ph_3PI_2 + 2\,In \longrightarrow InI_3(PPh_3)_2 \cdot InI_3(PPh_3)$$

$$3\,Pr^i_3PI_2 + 2\,In \longrightarrow 2\,InI_3(PPr^i_3)$$

The structure of the latter compound contains $InI_3(PPr^i_3)$ structural units, in which the indium atom is surrounded by three iodine atoms and the phosphorus atom of a phosphine group.[223]

This is consistent with the data on 1:1 phosphine complexes of indium triiodide with PBu^i_3, $PHPh_2$, $PHCy_2$, $PHBu^t_2$, PPh_3 and PCy_3 ligands,[224] which have the $R \cdot InI_3$ structural motif (X-ray diffraction data, IR, Raman and NMR spectroscopic data).

The reaction of aryllithium derivatives with Pr^iInI_2 or InI_3 in diethyl ether at a temperature of −78 to 25 °C affords organic In^{III} complexes *via* metal–metal exchange.[225]

$$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Li + RInI_2 \longrightarrow$$

$$\longrightarrow [2,6\text{-}(Me_2NCH_2)_2C_6H_3]InI(R)$$

R = I, Pr^i

$$[2\text{-}(Me_2NCH_2)C_6H_4]Li + RInI_2 \longrightarrow$$

$$\longrightarrow 2\text{-}(Me_2NCH_2)C_6H_4]InI(R)$$

R = I, Pr^i

In these complexes, In^{III} has the coordination number 5 (trigonal bipyramid) and 4 depending on the number of CH_2NMe_2 groups in the starting aryllithium molecule. The X-ray diffraction data [225] confirm the monomeric structure of the compound $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]InI_2$, the polymeric structure of the derivative $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]InI(Pr^i)$, which is composed of infinite zigzag chains, and the dimeric structure of the complexes $[2\text{-}(Me_2NCH_2)C_6H_4]InI(R)$ (R = I, Pr^i).

The reaction of InI_3 with di- or tridentate phosphine ligands produces complexes of different structural types depending on the ratio of the starting reagents.[226]

$$1,2\text{-}(Ph_2P)_2C_6H_4 + InI_3 \longrightarrow \{1,2\text{-}(Ph_2P)_2C_6H_4\}InI_3$$

$$1,2\text{-}(Ph_2P)_2C_6H_4 + 2\,InI_3 \longrightarrow [\{1,2\text{-}(Ph_2P)_2C_6H_4\}InI_2]^+[InI_4]^-$$

The latter compound undergoes solvolysis in the presence of THF, acetone and/or $P(O)Ph_3$ to form adducts of the former type,[226] for example:

$$[\{1,2\text{-}(Ph_2P)_2C_6H_4\}InI_2]^+[InI_4]^- \xrightarrow{Solv} \longrightarrow \{1,2\text{-}(Ph_2P)_2C_6H_4\}InI_3 + InI_3\cdot Solv$$

Solv = THF, Me_2CO, $P(O)Ph_3$

The reaction of $(2\text{-}Ph_2PC_6H_4)_2PPh$ with InI_3 yields $[\{2\text{-}Ph_2PC_6H_4)_2PPh\}InI_2]^+[InI_4]^-$ containing the four-coordinate central In^{III} atom, while no adducts containing the five-coordinate metal atom similar to the complex $\{1,2\text{-}(Ph_2P)_2C_6H_4\}InI_3$ are generated.[226] The crystal structure of these ionic complexes $[(L)InI_2]^+[InI_4]^-$ is entirely different from the structures of derivatives of bis(diphenylphosphino)ethane (dppe) and its disulfide ($dppeS_2$) synthesized in more recent studies. Thus, compounds with dppe and $dppeS_2$ have a molecular structure, the $I_3In\cdot dppe\cdot InI_3$ and $I_3In\cdot dppeS_2\cdot InI_3$ structural units being present both in the solid state and solutions.[227] The treatment of the complex $dppe\cdot InI_3$ with excess iodide anions leads to its decomposition and the formation of $[InI_4]^-$ ions.[228] A similar ligand exchange was observed for triphenylphosphine complexes of InI_3.[228] Naturally, the ligand exchange in In^{III} iodide complexes can occur in reactions with stronger complex-forming agents, such as crown ethers. For instance, the treatment of the adduct $InI_3\cdot Et_2O$ with crown ether in diethyl ether gives the complex $[InI_2(18\text{-crown-}6)]^+[InI_4]^-$, which is precipitated in 70% yield.[229]

The phosphine ligand $1,2\text{-}(Me_2P)_2C_6H_4$ and the arsine ligand of similar composition react with InI_3 in toluene (80 °C, 2 h) to give the complexes $[InI_2\{1,2\text{-}(Me_2E)_2C_6H_4\}]^+[InI_4]^-$ and $[InI_2\{1,2\text{-}(Me_2E)_2C_6H_4\}_2]^+[InI_4\{1,2\text{-}(Me_2E)_2C_6H_4\}]^-$ (E = P, As), respectively, depending on the ratio of the starting reagents.[230] These complexes contain six-coordinate In^{III} atoms. In the cations, these atoms are surrounded by two bidentate phosphine or arsine ligands and two iodide anions; in the anions, by four iodide anions and one bidentate ligand.

In the complex of InI_3 with 4-picoline with the composition $InI_3(4\text{-}MeC_5H_4N)_3$, the six-coordinate central indium atom has an octahedral coordination geometry with a meridional arrangement of three iodide and three picoline ligands in the vertices of the coordination polyhedron,[231] like in the tripyridine complex of InI_3.[232]

The complexes $InI_3\cdot PPh_3$ and $InI_3\cdot 2\,PPh_3$ contain four- and five-coordinate indium atoms surrounded by four (trigonal pyramid) and five (trigonal bipyramid) ligands.[228] A similar coordination (4 and 5) was observed in 1 : 1 and 1 : 2 complexes of InI_3 with 9-xanthone.[233]

The reaction of InI_3 with *o*- or *p*-quinone (Q) affords the derivative $[InI_2]^+Q^-$, which, in turn, reacts with excess picoline (pic) to form complexes $\{[InI_2]^+Q^-\}\,2\,pic$. In solutions, the complexes $[InI_2]^+Q^-$ form bridged structures.[234]

$$2\,[InI_2]^+Q^- \longrightarrow (Q)IIn(\mu\text{-}I)_2InI(Q)$$

However, the complexation of InI_3 with iminoquinone in the presence of sodium metal gives biradical chelate indium complexes containing five-coordinate In^{III}, which is coordinated by two radical anions and iodide (EPR and X-ray diffraction data); the Q_2InI structural unit has a tetragonal-pyramidal geometry.[235] A similar reaction with iminoquinone in toluene in the absence of sodium metal affords the five-coordinate In^{III} complex $QInI_3$ with the bidentate iminoquinone ligand (Q) (the coordination polyhedron of indium is a distorted trigonal bipyramid). However, the use of mixed-valence iodide $In^+[InI_4]^-$ (or In_2I_4) instead of InI_3 resulted in the formation of both complexes mentioned above. Piskunov *et al.*[235] attributed this fact to the disproportionation of In_2I_4 that was used in the reaction into InI and InI_3, which react separately with the ligands. Non-radical analogues of the complex Q_2InI were also synthesized by the reaction of indium(III) *o*-aminophenolates with alkyl iodides, resulting in the addition of alkyl groups to benzene rings at the *para* positions with respect to the nitrogen atoms; in this case, iodide anions complete the coordination polyhedron of indium to a tetragonal pyramid.[236]

The complex $QInI_3$ can react with 1,1,2,2-tetramethylethylenediamine (TMEDA) with replacement of one iodide ligand to give a six-coordinate In^{III} complex $QInI_2(TMEDA)$.[237]

In In^{III} iodide complexes with porphyrins, the central indium atom lies above the plane of the macrocyclic ligand and the iodine atom occupies an apical position (coordination polyhedron is a tetragonal pyramid).[238, 239] In solution, these complexes react with excess I^- ions to form anionic six-coordinate In^{III} complexes, in which both iodine atoms are at the same side with respect to the plane of the macrocyclic ligand.[238]

IV.2. Indium(I) and indium(II) complexes

One of the first characterized organic indium(I) complexes was the compound $[InMe_2]^+[InI_4]^-$. It was synthesized by the reaction of excess methyl iodide with indium monoiodide in the absence of a solvent (25 °C, 1 h, 100% yield) by Gynane, Waterworth and Worrall[240, 241] and also by Poland and Tuck[242] in 1972. The authors characterized this compound by vibrational spectroscopy[240–242] and mass spectrometry[242] and suggested the linear structure of the $[InMe_2]^+$ cations.

Contreras *et al.*[218] synthesized complexes of In^I and In^{III} iodides with *N*,*N*′-dimethyl-4,4′-bipyridine with the compositions $(Me_2bipy)In^II_3$ and $(Me_2bipy)In^{III}I_5$, respectively, by the reaction of indium with bipyridinium iodide in methanol

under an argon atmosphere at room temperature over 2–3 h. The use of $In[InI_4]$ as the reactant gives rise to the In^{I} and In^{III} complexes with bipyridine mentioned above.[218] As it was shown by IR and Raman spectroscopy, $[InI_3]^{2-}$ groups with the C_{3v} symmetry are present in the crystal lattice of the In^{I} complexes.

Indium(I) complexes, in which the monovalent indium cation is not the central atom, would be expected to exist. The complex $In^{I}[In^{III}I_4]$ can be quite easily transformed into other In^{III} complexes by solvolysis in diethyl ether. Actually, Freeland and Tuck[34] described the preparation of $In[InI_4]$ by the reaction of the metal (indium foil) taken in excess with elemental iodine in toluene (heating under reflux, 18 h). The diiodide was transformed into $InI_3 \cdot Et_2O$ and indium monoiodide by means of solvolysis in excess diethyl ether.[34] The structures of the compounds[243] and their composition were determined by chemical analysis and vibrational spectroscopy.

Complexes of indium in low oxidation states with such organic cations as $[Bu^{n}_4N]^+$ show a different behaviour.[244] The mixed-valence diiodide $In[InI_4]$ reacts with Bu^{n}_4NI in xylene under reflux to give the complex $(Bu^{n}_4N)_2In_2I_6$, which contains $[In_2I_6]^{2-}$ anions composed of equivalent In^{II} atoms (rather than the mixed-valence In^{I}/In^{III} compound). Similar results were obtained in the reaction of InI_3 with $(Me_2bipy)^{2+}[InI_3]^{2-}$ in dry methanol.[244]

Similarly, the reaction of InI and InI_3 with TMEDA in a toluene–dichloromethane mixture at −20 °C (Ref. 245) produces the divalent indium complexes $(TMEDA)_2In_2I_4$ with a metal–metal bond in I_2InInI_2 moieties. The related In_2BrI_3 and In_2IBr_3 fragments were generated in the the reactions involving indium iodide and bromide, respectively.[245]

Clarkson *et al.*[246] synthesized In^{I} iodide complexes by the reaction of InI and/or InI_3 with the appropriate iron carbonyl compound in THF.

$$InI_3 + 2\,Na[Fe(CO)_2(\eta^5\text{-}Cp)] \longrightarrow InI[Fe(CO)_2(\eta^5\text{-}Cp)]_2$$

$$InI + Fe(CO)_2(\eta^5\text{-}Cp)_2 \longrightarrow InI[Fe(CO)_2(\eta^5\text{-}Cp)]_2$$

$$InI\,[Fe(CO)_2(\eta^5\text{-}Cp)]^+ + [Et_4N]^+I^- \longrightarrow$$
$$\longrightarrow [Et_4N]^+\,[InI_2\{Fe(CO)_2(\eta^5\text{-}Cp)\}_2]^-$$

$$InI[Fe(CO)_2(\eta^5\text{-}Cp)]_2 + PMe_2Ph \longrightarrow$$
$$\longrightarrow InI(PMe_2Ph)\,[Fe(CO)_2(\eta^5\text{-}Cp)]_2$$

As it was shown by vibrational spectroscopy, the complex $InI[Fe(CO)_2(\eta^5\text{-}Cp)]_2$ contains the square In_2I_2 unit, in which the indium atoms are additionally coordinated by two iron atoms (*i.e.*, the coordination number of indium is 4); while $InI(PMe_2Ph)\cdot[Fe(CO)_2(\eta^5\text{-}Cp)]_2$ contains four-coordinate indium ions (coordination polyhedron includes one iodine, one phosphorus and two iron atoms).[246]

The reaction of equimolar amounts of AlI_3, elemental iodine and $[InC(TMS)_3]_4$ (TMS = $SiMe_3$), in which tetrahedral In_4 units coordinated by $C(TMS)_3$ groups are attached to the indium atoms, in hexane at room temperature followed by heating at 80 °C for 5 min affords the bridged complex $(\mu\text{-}I)_2[InC(TMS)_3]_3$ in 73% yield.[247] In this complex, one $InC(TMS)_3$ group of the initially tetrahedral unit is removed and replaced by two iodine atoms attached to two terminal indium atoms. Two In—In bonds in the $(\mu\text{-}I)_2[InC(TMS)_3]_3$ structure remain unchanged (single-crystal X-ray diffraction).

The reaction of $Pr^{n}_3PI_2$ with indium metal (diethyl ether, room temperature, N_2, 2 days) produces the dimer $[InI_2(PPr^{n}_3)]_2$ with a metal–metal bond.[223]

The structures of some recently synthesized complexes of lower indium iodides with organic ligands involve polymetallic clusters.

In particular, the treatment of an equimolar mixture of InI and β-diketimine (*N*-[4-(3,5-dimethylphenylamino)pent-3-en-2-ylidene]-3,5-dimethylphenylamine) with $(TMS)_2$ in THF at −78 °C resulted in the precipitation of the complex $I[In\{N(3,5\text{-}Me_2C_6H_3)C(Me)\}_2CH]_6I$.[248] This complex contains six indium atoms linked by metal–metal bonds to form a chain. In addition, each indium atom is coordinated by the chelate diimine ligand; the terminal indium atoms are additionally coordinated by iodide anions.

Indium monoiodide disproportionates when mixed with 2 equiv. of TMEDA (12% solution in toluene) at −50 °C.[249]

$$8\,InI + 4\,TMEDA \longrightarrow$$
$$\longrightarrow (TMEDA)I_2In\text{–}In[InI(TMEDA)]_2\text{–}InI_2\text{–}InI_2(TMEDA) + 2\,In\ (metal)$$

Six indium atoms form the $In_3In\text{–}In\text{–}In$ skeleton (the structure was established by X-ray diffraction).[249]

A similar disproportionation was observed in the synthesis of the complex $[(MeGa(pz)_3)_2In]^+[InI_4]^-$ starting from InI in THF at −30 °C.[223] This complex contains the six-coordinate indium atom in an octahedral environment formed by six pyrazole nitrogen atoms of two tridentate ligands. Meanwhile, the oxidation state of In^{I} in the related compound $\{HB(3,5\text{-}Me_2\text{-}pz)_3\}_2InI$ that was synthesized under similar conditions remains unchanged.[221]

V. Organometallic compounds of indium iodides

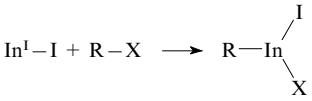
Organometallic compounds of indium have been the subject of several reviews,[5–8,27,28] but no special attention was given to indium iodides. This Section will endeavour to fill this gap and will be focused on organic indium iodides. Chemical transformations, in which indium iodides are involved as reactants or, more frequently, as catalysts, will be considered.

Like inorganic halides, organic compounds of indium iodides are covered in the literature in much less detail compared to the corresponding organic derivatives of indium chlorides and bromides. Evidently, this is due to the differences in the chemical and physical properties of the corresponding halides. Thus, indium iodides are more sensitive to moisture, atmospheric oxygen, *etc.*

A large body of investigations concerned with organic indium iodides was performed and published in the past decade. In 1993, Tuck[27] mentioned only inorganic and organic complexes of indium iodide. In 2004, Peppe[5] explicitly pointed out that organic derivatives of indium were barely used.

The triiodide InI_3 is more rarely applied as a reactant or a catalyst compared to InI. This is due to the specific ability of InI to be involved in certain chemical reactions, in particular, to be inserted into carbon–heteroatom covalent bonds (Scheme 1).[250–265] It should be noted that similar reactions with InCl and InBr also proceed.[7,8]

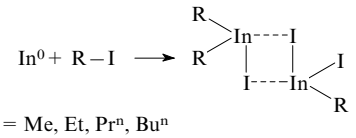
Scheme 1



X = Hal, O-, Si-, B-containing moiety, *etc.*

Indium can form sesquihalides. These *in situ* generated derivatives are intermediates in a series of indium-catalyzed reactions (Scheme 2).[266]

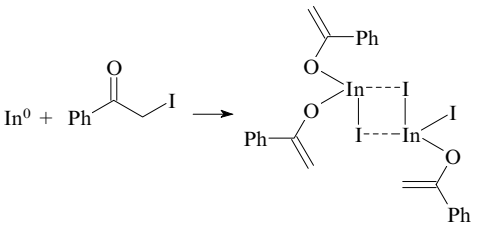
Scheme 2



R = Me, Et, Pr^n, Bu^n

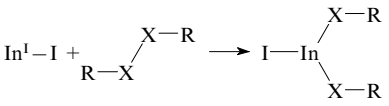
Araki and Butsugan[251] described structurally similar enolates $(RO)_2InI_2In(I)OR$, which have chemical properties similar to those of the derivatives RIn(I)X (Scheme 3).

Scheme 3



The reduction of dichalcogenides with indium iodide(I) affords indium(III) iodide dichalcogenides (Scheme 4).[6, 27, 259, 261, 267 – 271]

Scheme 4



X = O, S, Se, Te

These dichalcogenides can be isolated in the individual form[272 – 274] or as complexes with organic ligands, *e.g.*, with pyridine.[219]

An important distinguishing feature of the reactions presented in Schemes 1 and 4 is the oxidation of In^I to In^{III}. Besides, indium organic compounds RIn(I)X and $IIn(XR)_2$ can be used as nucleophiles without isolation (purification) in the course of the *in situ* generation in the reaction system.

Historically, investigations of organic compounds of indium iodides were started since the 1970s after the publication by Waterworth and Worrall[275] of the reaction of anhydrous methyl bromide with indium(I) monobromide.

$$MeBr\ (anhydr.) + InBr \longrightarrow MeInBr_2$$

The mass spectrometric data attested to the formation of dimeric molecules $(MeInBr_2)_2$. Gynane *et al.*[276] also observed the insertion of indium bromide into methyl iodide giving a mixture of products with an indium – carbon bond (the line at 518 cm^{-1} in the Raman spectrum).

A year later, Poland and Tuck[242] published more detailed results and described the formation of indium(III) organic derivatives according to Scheme 1 and also products with different stoichiometry, which were synthesized by varying the ratio of the reactants. The authors determined different structures of the products $RInI_2$ (R = Me, Et, Pr^n, Bu^n). The methyl derivatives were considered as ionic compounds having the structure $[Me_2In]^+[InI_4]^-$; whereas the other alkyl derivatives were considered as dimers $(RInI_2)_2$ with a *cis* configuration of $R(I)InI_2In(I)R$. In the studies cited,[242, 275] the samples were characterized by mass spectrometry, IR spectroscopy and Raman spectroscopy. The ionic nature of $[Me_2In]^+[InI_4]^-$ was additionally confirmed by electrical conductivity measurements in nitromethane.[242] The Raman spectra recorded in these studies[242, 275] are somewhat different in the low-frequency region but are otherwise in agreement. However, Poland and Tuck[242] suggested the *cis* configuration of the $R(I)InI_2In(I)R$ molecule, whereas the *trans* conformation or a mixture of *cis* and *trans* isomers was stated by Gynane and co-workers.[241, 276] The oligomeric character of the particles (tetramers) in $(EtInI_2)_2$ vapour was also mentioned.[241]

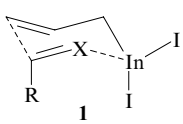
In further investigations, Gynane, Waterworth and Worrall prepared and isolated dioxane complex adducts of $RInI_2$ (R = All, Bn)[243] and synthesized indium organic compounds with different compositions: $R_2InI_2In(I)R$ and R_2InI.[266] Contreras and Tuck[214] synthesized cyclopentadienyl derivatives of indium(III), $(\eta^5\text{-Cp})InI_2$ and $(\eta^5\text{-Cp})_2InI$, using different reactions. Chao and Rieke[277] demonstrated that indium metal can be employed instead of indium halides for the preparation of organic derivatives of indium iodide.

V.1. Insertion of indium monoiodide into carbon – heteroatom bonds and reactions of intermediates RIn(I)X

Indium monoiodide has been used for decades as a catalyst and co-catalyst for various organic reactions, including alkylation (in particular, allylation), cleavage of heterocycles and so on. When discussing the mechanisms of the corresponding reactions, it is generally assumed that InI is inserted into a carbon – heteroatom bond, *e.g.*, into a C – I bond, to form $RInI_2$ in reactions with alkyl iodides followed by a transformation of organoindium intermediates. Examples of reactions catalyzed by indium monoiodide are given in Table 4. It should be noted that, although Araki and Butsugan[251] hypothesized that the reaction proceeds through indium enolates as intermediates, the mechanism involving the insertion into a carbon – heteroatom bond seems to be more probable.

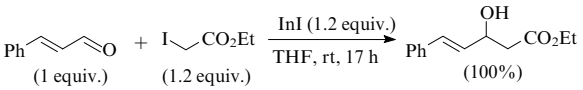
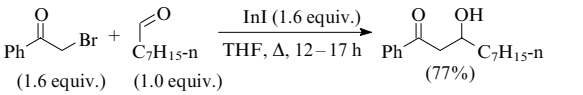
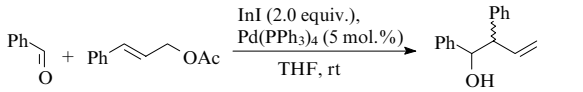
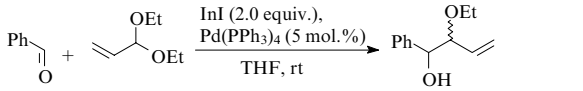
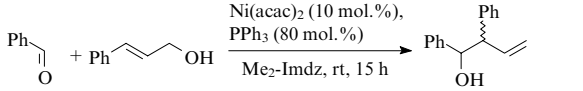
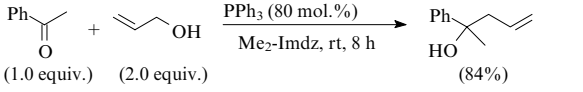
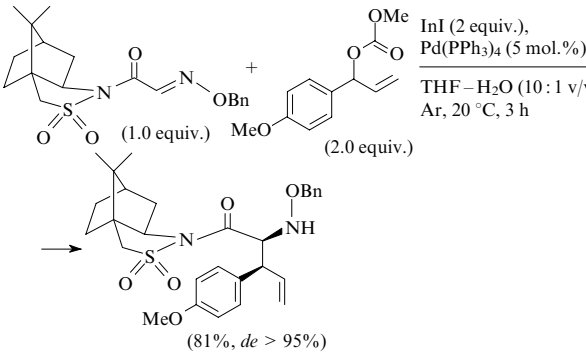
Detailed investigations of organic indium halides RIn(I)X demonstrated that these compounds are prone to react with compounds containing (C=C, C=O, C=N) double bonds or (C≡C, C≡N) triple bonds or with their derivatives (*e.g.*, acetals) (see Table 4). Apparently, the reaction proceeds through a six-membered transition state corresponding to the Zimmerman – Traxler model (Structure **1**). This assumption is based on the observed regio- and stereochemistry of the reaction products (Scheme 5).

Structure 1



1

Table 4. Examples of reactions involving the insertion of indium(I) monoiodide into a carbon – non-metal bond and the reaction of *in situ* generated indium(III) compounds with C-electrophiles.

Reaction	Ref.
a) Reformatsky C-alkylation of aldehydes	
 (1 equiv.) (1.2 equiv.) InI (1.2 equiv.), THF, rt, 17 h → (100%)	250
 (1.6 equiv.) (1.0 equiv.) InI (1.6 equiv.), THF, Δ, 12 – 17 h → (77%)	251
b) Pd^0-Catalyzed C-allylation of aldehydes with allyl esters, alcohols, carbonic acid esters, halides, phenol ethers, thioethers, etc.	
 (1.0 equiv.) (2.0 equiv.) InI (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, rt → (100%, *syn* : *anti* = 14 : 86)	252
c) Pd^0-Catalyzed C-allylation involving acetals	
 (2.0 equiv.) (1.0 equiv.) InI (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, rt → (91%, *syn* : *anti* = 64 : 36)	252
d) C-Allylation of aldehydes and ketones catalyzed by Ni compounds	
 (1.0 equiv.) (2.0 equiv.) InI (2.0 equiv.), $Ni(acac)_2$ (10 mol.%), PPh_3 (80 mol.%), Me_2-Imdz, rt, 15 h → (98%, *syn* : *anti* = 15 : 85)	253
 (1.0 equiv.) (2.0 equiv.) InI (2.0 equiv.), $Ni(acac)_2$ (10 mol.%), PPh_3 (80 mol.%), Me_2-Imdz, rt, 8 h → (84%)	254
e) Pd^0-Catalyzed C-allylation of aldoximes involving carbonic and acetic acid esters	
 (1.0 equiv.) (2.0 equiv.) InI (2 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF – H_2O (10 : 1 v/v), Ar, 20 °C, 3 h → (81%, *de* > 95%)	254

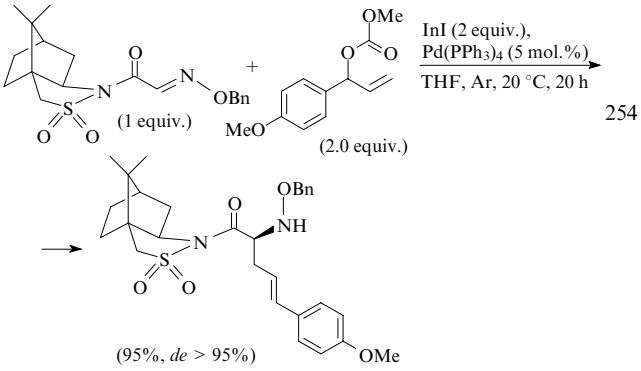
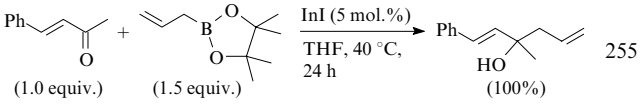
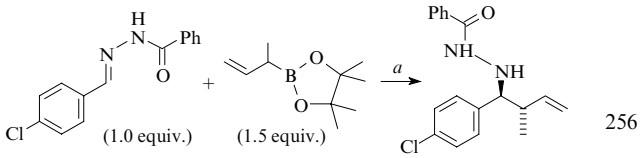
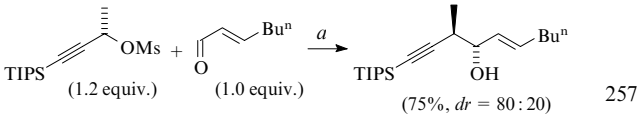
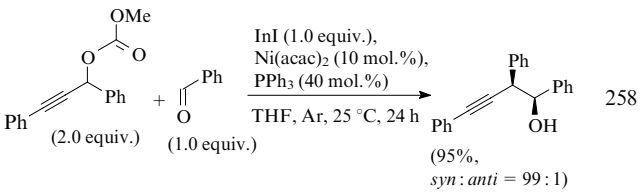
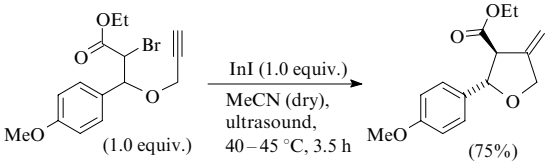
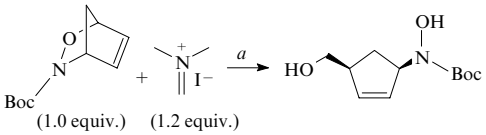
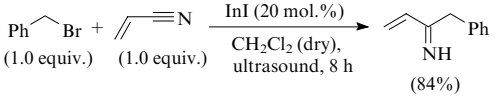
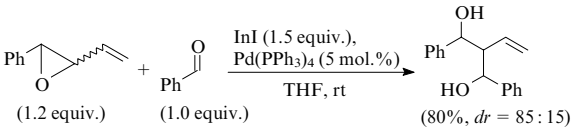
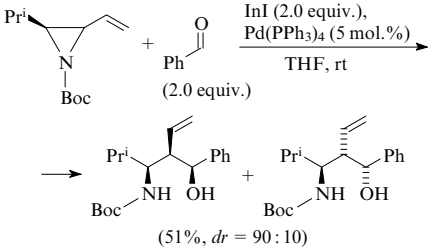
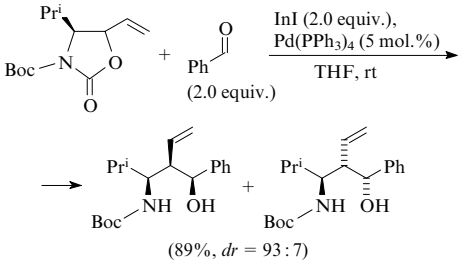
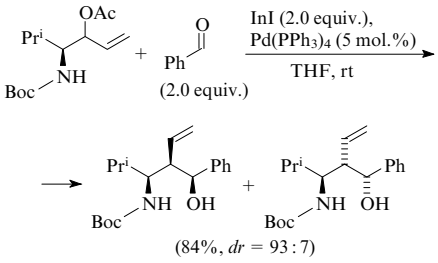
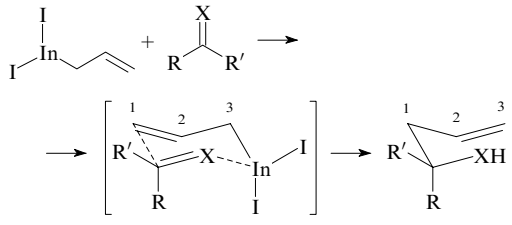
Reaction	Ref.
e) Pd^0-Catalyzed C-allylation of aldoximes involving carbonic and acetic acid esters	
 (1 equiv.) (2.0 equiv.) InI (2 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, Ar, 20 °C, 20 h → (95%, *de* > 95%)	254
f) C-Allylation of ketones with allyl boronates in the absence of a Pd or Ni catalyst (i.e., in the presence of only the added or in situ generated indium monoiodide and/or its mixture with InI_3)	
 (1.0 equiv.) (1.5 equiv.) InI (5 mol.%), THF, 40 °C, 24 h → (100%)	255
g) C-Allylation of hydrazones with allyl boronates in the absence of a Pd or Ni catalyst (only an In^I catalyst)	
 (1.0 equiv.) (1.5 equiv.) *a* → (100%, regioselectivity > 99%, *syn* : *anti* = 4 : 96) (*a*) InI (5 mol.%), Pr^iOH (5.0 equiv.), CH_2Cl_2, 0 °C, 24 h	256
h) Pd^0-Catalyzed C-propargylation of aldehydes	
 (1.2 equiv.) (1.0 equiv.) *a* → (75%, *dr* = 80 : 20) (*a*) InI (1.6 equiv.), $Pd(OAc)_2$ (6 mol.%), PPh_3 (6 mol.%), HMPA (excess), THF, 0 – 25 °C, 1.25 h	257
i) Ni-Catalyzed C-propargylation of aldehydes	
 (2.0 equiv.) (1.0 equiv.) InI (1.0 equiv.), $Ni(acac)_2$ (10 mol.%), PPh_3 (40 mol.%), THF, Ar, 25 °C, 24 h → (95%, *syn* : *anti* = 99 : 1)	258

Table 4 (continued).

Reaction	Ref.
j) Intramolecular C-propargylation accompanied by ring closure of propargyl ethers in the absence of Ni and/or Pd catalysts (accompanied by elimination of a bromine atom at the β-position with respect to the ether O atom) [a]  (1.0 equiv.) InI (1.0 equiv.), MeCN (dry), ultrasound, 40 – 45 °C, 3.5 h (75%)	259
k) C-Allylation of Vilsmeier reagent accompanied by the ring opening  (1.0 equiv.) (1.2 equiv.) (*a*) InI (1.2 equiv.), $Pd_2(dba)_3$ (10 mol.%), PPh_3 (30 mol.%), THF – H_2O (9 : 1)	260
l) Ultrasound-assisted regioselective C-allylation, benzylation and homobenzylation of α,β-unsaturated nitriles with organic bromides in the presence of only indium monoiodide as a catalyst  (1.0 equiv.) (1.0 equiv.) InI (20 mol.%), CH_2Cl_2 (dry), ultrasound, 8 h (84%)	261
m) Pd-Catalyzed regio- and stereoselective epoxide ring opening followed by the reaction with aldehydes  (1.2 equiv.) (1.0 equiv.) InI (1.5 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, rt (80%, *dr* = 85 : 15)	252
n) Pd-Catalyzed regio- and stereoselective aziridine ring opening  (2.0 equiv.) InI (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, rt (51%, *dr* = 90 : 10)	262
o) Pd-Catalyzed regio- and stereoselective cleavage of the five-membered oxazolidinone ring followed by the reaction with aldehydes  (2.0 equiv.) InI (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, rt (89%, *dr* = 93 : 7)	262
p) Replacement of acetoxy groups with aldehydes  (2.0 equiv.) InI (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol.%), THF, rt (84%, *dr* = 93 : 7)	262

Note. The following abbreviations are used: rt is room temperature, acac is acetylacetonate, Me_2-Imdz is 1,3-dimethylimidazolidin-2-one, TIPS = Pr^i_3Si, Ms = $MeSO_2$, HMPA is hexamethylphosphoramide, dba is dibenzylideneacetone, Boc = $Bu^tOC(O)$.
[a] Ranu and Mandal [259] reported evidence for a radical reaction mechanism.

Scheme 5



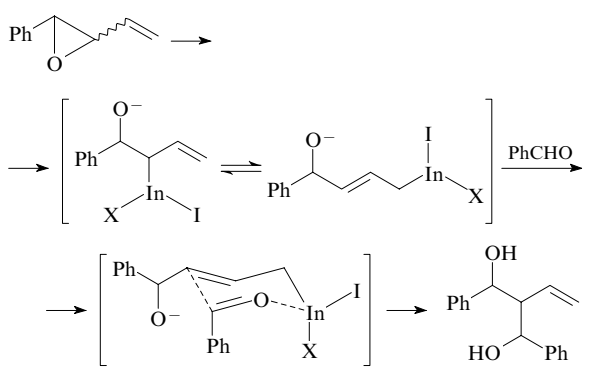
X = CR''_2, NR'', O; R'' are H or other substituents

Hirashita *et al.*[253] disclosed the role of In^I mediators (insertion into a carbon – heteroatom bond in the initial reaction step) by demonstrating that the use of trivalent indium compounds, such as $InCl_3$ or $In(OH)_3$, instead of monovalent indium compounds, as well as attempts to perform C-allylation of a carbonyl compound in the presence of a Ni catalyst but without using an In reactant, were unsuccessful because intermediate Zimmerman – Traxler structures are not formed under these conditions.

Extensive additional evidence for this mechanism was published in the literature (see Table 4). Schneider and Kobayashi [7] reported that the reaction that proceeds through the formation of an organoindium intermediate can afford a complex allylic In intermediate, which than reacts with another molecule to form the above-mentioned six-membered Zimmerman – Traxler transition state. Schneider, Kobayashi and Konishi [255, 256] and also Chao and Rieke [277] suggested that this complex can undergo an internal rearrangement accompanied by migration of the indium atom, which accounts for the formation of α-allyla-

tion products rather than expected γ-allylation products (Scheme 6).

Scheme 6



Experiments using deuterium-labelled reagents and indium(I) trifluoromethanesulfonate as the catalyst instead of indium monoiodide [7] confirmed the proposed mechanism of the rearrangement (Scheme 7).

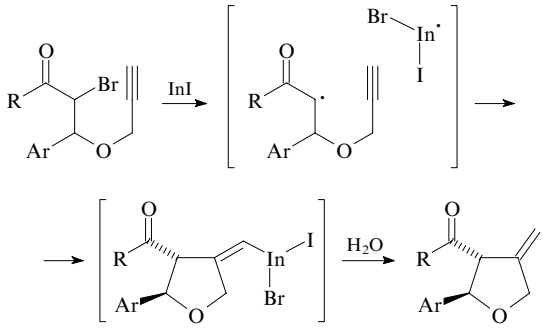
The above is consistent with the earlier results reported by Miyabe *et al.*,[254] who also discussed a similar rearrangement of allylic In intermediates, which they observed in an aqueous medium in the course of C-allylation of oximes (see the reactions *e* in Table 4) (Scheme 8).

Other examples of regio- and stereoselectivity of indium(I) iodide-mediated reactions are given in Table 4.

The stereochemistry of such reactions in the presence of chiral ligands was investigated by Chakrabarti *et al.*[278] in relation to the asymmetric allylation of hydrazones in the presence of InI (similar reactions are presented in Table 4, reaction *g*).

A different reaction mechanism was proposed by Ranu and Mandal,[259] who studied the cyclization of α-bromo-β-propargyloxy ketones and esters and demonstrated that this reaction proceeds through the formation of an intermediate radical (Scheme 9). This is the only publication,where an alternative mechanism was proposed.

Scheme 9



R = Me, OMe, OEt

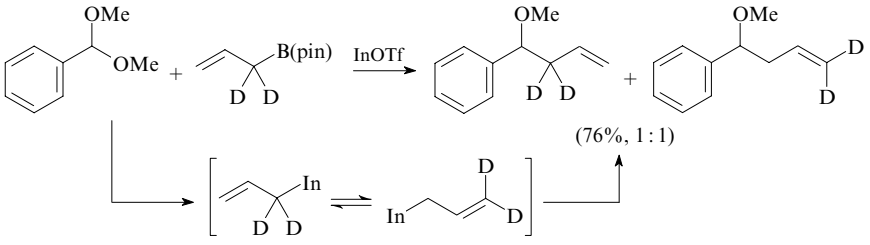
This mechanism is evidenced by the fact that the reaction was completely terminated in the presence of radical scavengers (*e.g.*, 2,2,6,6-tetramethylpiperidinoxyl or *p*-benzoquinone).[259]

V.3. Reactions involving the *in situ* formation of organic indium sesquiiodides and their reactions with substrates containing double and triple bonds

Since the first reference [266] to indium sesquiiodides in 1974 and up to the present time, their structures as individual compounds have not been ultimately established. In later publications,[279–284] these compositions were used without the isolation of organoindium derivatives that were generated *in situ* (Table 5). However, regardless of the actual structure of these compounds in solution, they show similar behaviour towards other substrates. The *in situ* generated organic indium iodides readily enter into Markovnikov-type reactions with unactivated alkynes to form alkenes with a terminal double bond.[281, 282] It should be noted that this addition is reversible in the case of trimethylsilylacetylene, the addition of which occurs at the terminal carbon atom of the alkyne system.[282]

The most vivid example is the directing ability of the hydroxy group of unsaturated (alkenic) alcohols.[283] Thus, the addition of organic indium derivatives to norbornene

Scheme 7



pin is pinacolyl

Scheme 8

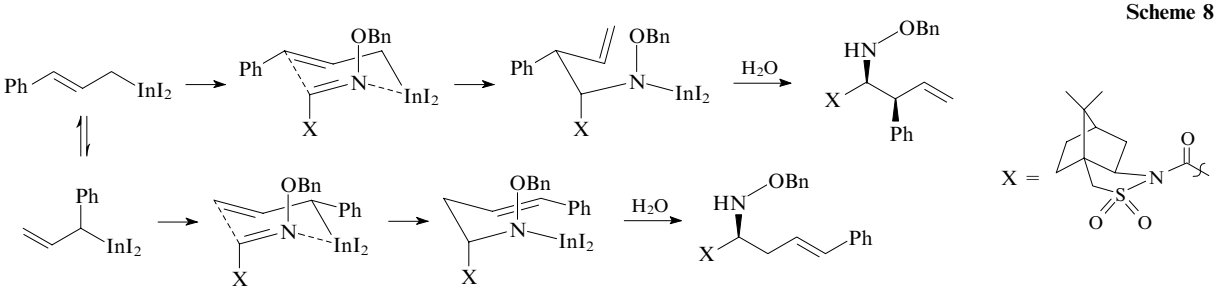
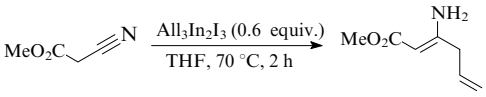
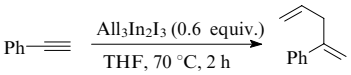
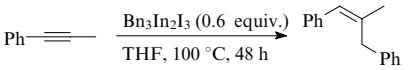
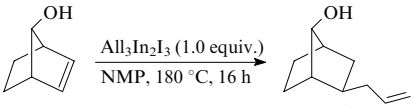
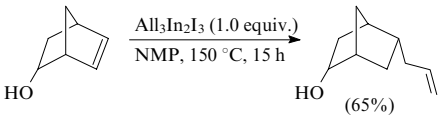
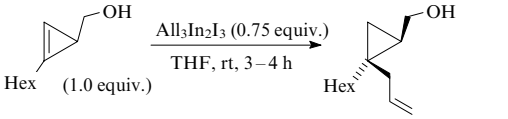
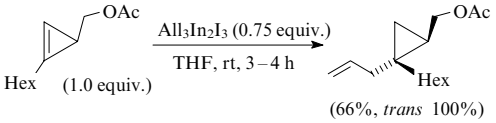


Table 5. Reactions of indium metal with alkyl halides accompanied by the *in situ* formation of indium(III) sesquiiodides followed by the addition to the double and/or triple bond.

Reaction	Ref.
a) Regio- and stereoselective addition to C≡C and C≡N triple bonds	
 (100%, *Z* 100%)	281, 282
 (94%)	282
 (64%, *Z* : *E* = 85 : 15)	282
($All_3In_2I_3$ and $Bn_3In_2I_3$ were synthesized *in situ* by the reaction of 1.2 equiv. of powdered In^0 (met.) with 1.8 equiv. of AllI or BnI in THF, rt, 1 h)	
b) Regio- and stereoselective addition to the C=C double bond	
 (72%)	283
 (65%)	283
($All_3In_2I_3$ was synthesized *in situ* by the reaction of 1.0 equiv. of powdered In^0 (met.) with 1.5 equiv. of AllI in *N*-methylpyrrolidone, rt, 0.5 h)	
 (95%, *cis* : *trans* = 93 : 7)	284 – 286
 (66%, *trans* 100%)	284 – 286
[$All_3In_2I_3$ was synthesized *in situ* by the reaction of powdered In^0 (met.) with an appropriate amount of AllI in THF]; Hex = n-C_6H_{13}	

alcohols usually occurs at the *cis* position with respect to the OH group (see Table 5). This selectivity is observed also for cyclopropene alcohols.[284 – 286] However, the selectivity changes for the *trans* addition if the OH group is protected by an acetyl group evidently due to steric hindrance.

V.4. Insertion of indium iodide into chalcogen – chalcogen bonds

Investigations of the insertion of monovalent indium into chalcogen – chalcogen bonds date back to 1984, when Peppe and Tuck[219] studied the reactions of peroxides, disulfides and diselenides with InI and isolated the corresponding indium compounds as their pyridine complexes. Later on, Tuck and co-workers[272] characterized the individual compounds $InI(XPh)_2$ (X = S, Se) by classical means, *i.e.*, they determined the melting points, performed elemental analysis and so on. Peppe and co-workers[273, 274] developed a simple and fast method for the synthesis of $InI(SePh)_2$ in dichloromethane at room temperature.

Some authors (see, for example, Refs 270, 271 and 287 – 292) employed $InI(XR)_2$ as the *in situ* generated chalcogenide nucleophiles instead of their isolation/purification as intermediate products (Table 6) [this is the case not only with selenides but also with related tellurium compounds $InI(TePh)_2$,[291] which show chemical properties similar to those of $InI(XPh)_2$ (X = S, Se)].

The use of stoichiometric amounts of InI, diselenides and/or disulfides in anhydrous dichloromethane allows the synthesis of unsymmetrical chalcogenides (see Table 6).[270, 274, 287] These reactions may be accompanied by the regioselective ring opening of epoxides,[268, 274] aziridines,[288, 292] oxazolines[289] and/or other chemical rearrangements. It should be noted that the palladium-catalyzed regioselective selenation (telluration) of alkynols in the presence of InI as a mediator affords (*Z*)-selenides (tellurides);[273, 291] the palladium-catalyzed InI-mediated vinylation of chalcogenides with the appropriate starting vinyl bromide, which is also a stereospecific reaction, gives exclusively *E*-products from the *E*-reactants and a mixture of *E*- and *Z*-products from *Z*-reactants[271] (see reactions *h* in Table 6).

V.5. Reactions catalyzed by indium iodide(III)

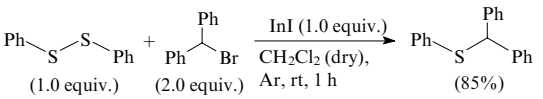
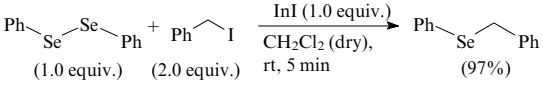
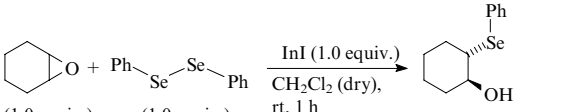
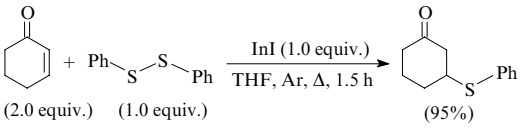
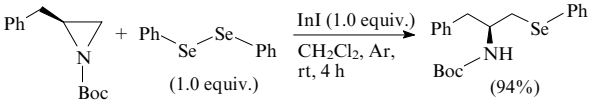
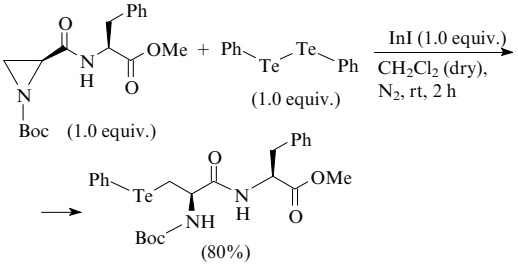
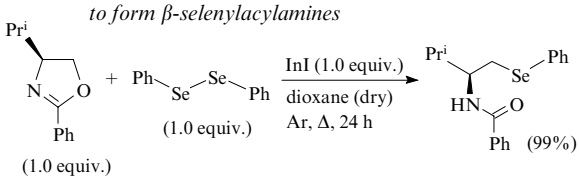
As opposed to indium monoiodide, the functions of InI_3 are restricted exclusively to the catalytic activity as a Lewis acid and are not related to the above-described reactions proceeding in the presence of InI (Table 7).

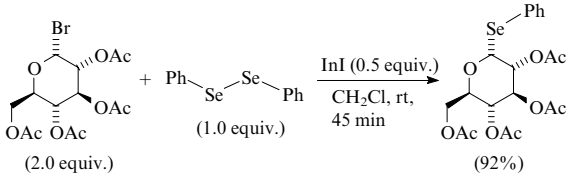
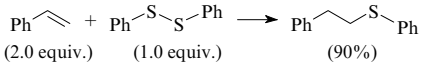
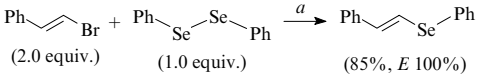
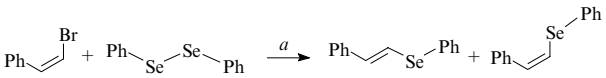
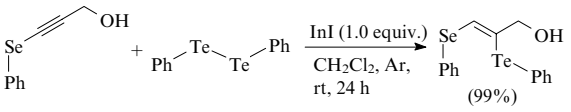
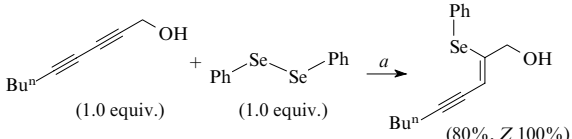
The Strecker cyanoamination (see reaction *a* in Table 7) in the presence of InI_3 can be performed under different conditions, including in the absence of a solvent;[293] meanwhile, the use of water as the reaction medium leads to a sharp increase in the reaction rate compared, for example, with the reaction in acetonitrile (the reaction time is 0.5 and 24 h, respectively). The reaction proceeds in two steps to form *in situ* imine as an intermediate in the first step. Then the cyano group of TMSCN adds to the C=N double bond of the resulting imine. In this transformation, iodide InI_3 acts as a Lewis acid-type catalyst and can be replaced with other indium(III) salts with retention of the efficiency of the reaction.

Similarly, InI_3 exhibits a Lewis acid-type catalytic activity in the regioselective C-methylation of 2,3-dimethylbutane with methanol to form tryptan (see reaction *b* in Table 7) and can also be replaced with other metal iodides having similar properties.[294, 295] However, InI_3-mediated reactions give products in higher yields compared to reactions in the presence of other metal iodides, *e.g.*, ZnI_2.[294]

Bsides, the catalysis using InI_3 provides a high yield in the cyclization of hydroxylated 1,5-allenynes (see reactions *c* in Table 7).[296] Corey and co-workers[297 – 299] performed different cyclization reactions catalyzed directly by InI_3 or by the generated InI_2^+ cations (see Table 7). These transformations involve the simultaneous formation of several fused rings from the starting alkyne polyenes. Similarly, InI_3 catalyzes the conversion of alkynediols to the corresponding bridged ketals.[299]

Table 6. Cleavage of chalcogen – chalcogen bonds in reactions of indium monoiodide followed by nucleophilic reactions of *in situ* generated indium(III) chalcogenides.

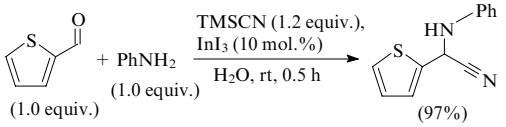
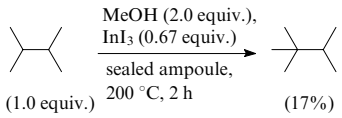
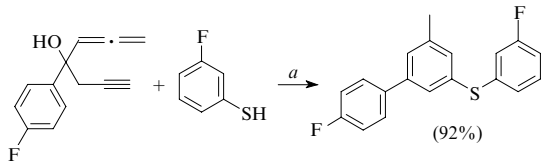
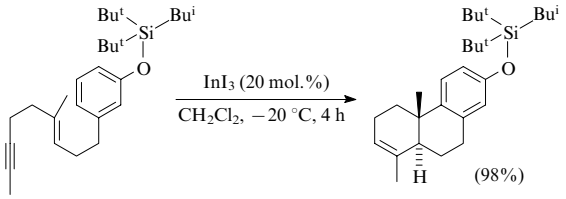
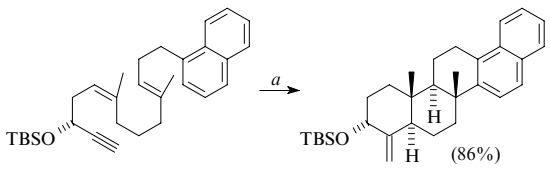
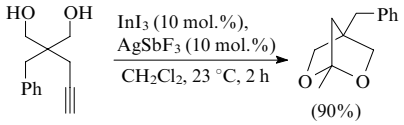
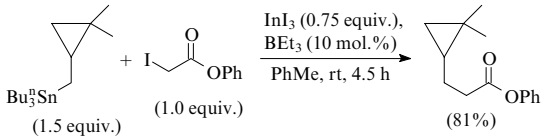
Reaction	Ref.
a) Synthesis of unsymmetrical chalcogenides	
	270
	287
b) Epoxide ring opening	
	274
c) Michael addition to unsaturated ketones and aldehydes	
	268, 271
d) Aziridine ring opening	
	288
	292
e) Oxazoline ring opening in the reaction with InI(SeR)$_2$ to form β-selenylacylamines	
	289
[similar direct oxygen nucleophilic substitution in the reaction with disulfides (> 90% yield) and ditellurides (25% yield)]	

Reaction	Ref.
f) Selenation of glycosyl bromides with IIn(XR)$_2$	
	290
(reaction proceeds *via* the S_N1 mechanism with retention of the α/β-stereochemistry of the carbon atoms C1) (there is also one example with chloride)	
g) Zinc-catalyzed anti-Markovnikov nucleophilic addition to styrenes	
	267
h) Use of IIn(XR)$_2$ in the Pd-catalyzed substitution (vinylation)	
	269
(*a*) InI (0.5 equiv.), $Pd(PPh_3)_4$ (1.5 mol.%), THF (dry), rt, 2.5 h	
	
(*a*) In (1.0 equiv.), $Pd(PPh_3)_4$ (1.5 mol.%), THF (dry), rt, 2.5 h (similar reaction with disulfide)	
i) Regio- and stereospecific hydrotelluration and hydroselenation of propargyl alcohols (anti-addition)	
	291
	273
(*a*) InI (1.0 equiv.), CH_2Cl_2 (dry), rt, 24 h	

It should be noted that InI_3 showed unusual catalytic activity in the reaction of tin(IV) cyclopropylmethyl compounds with phenyl iodoacetates (see Table 7 *d*).[300] This reaction is accompanied by the opening and closure of cyclic structures to form *in situ* intermediate homoallylic diiodo derivatives of indium(III), which can be identified by studying linear by-products.

Therefore, based on the data on organoindium compounds considered above, one would expect that these compounds will continue to attract increasing interest of synthetic chemists, resulting in an increase in the number of publications, in which researchers will use organic compounds of indium (formed *in situ* or generated as intermedi-

Table 7. Reactions catalyzed by indium iodide(III).

Reaction	Ref.
a) Strecker cyanoamination	
	293
b) Regioselective C-methylation	
	294, 295
c) Ring formation (including the formation of several rings)	
	296
	297, 298
	299
	299
d) Coupling reactions accompanied by opening and closure of cyclopropane moieties	
	300

ates without isolation and/or purification) like Grignard reagents.

VI. Indium monoiodide as a far-IR optical material

An interest in indium monoiodide as a photonic material is reflected in recent publications.[46, 120, 301 – 306] Chinese researchers [301] synthesized InI powder by the double-temperature zone vapour transporting method starting from high-purity reactants In (7N) and I_2 (5N). Single crystals for radiation detectors were grown by the Czochralski method.[302]

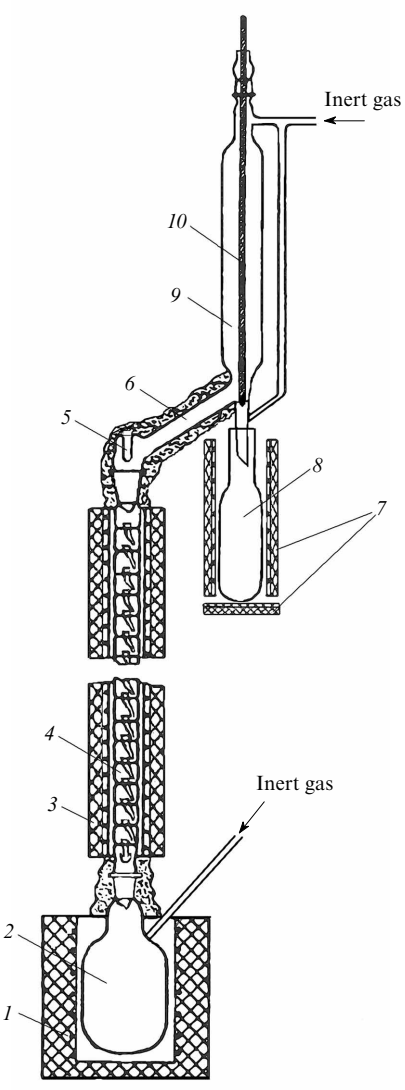


Figure 14. Schematics of a fractional distillation setup for InI.[46] (*1*) Furnace, (*2*) reboiler, (*3*) column heater, (*4*) fractional distillation column, (*5*) thermocouple pocket, (*6*) pipe, (*7*) receiver heaters, (*8*) receiver, (*9*) condenser, (*10*) needle collector.



Figure 15. External shape of an InI single crystal.[304]

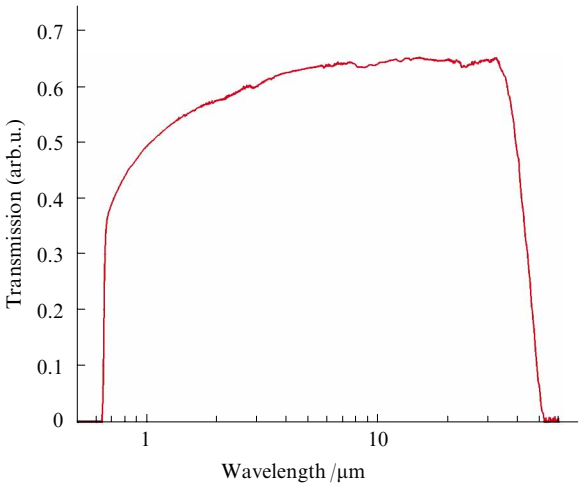


Figure 16. Transmission spectrum of a polished single-crystal wafer of InI.[304] The wafer thickness is 1.80 mm.

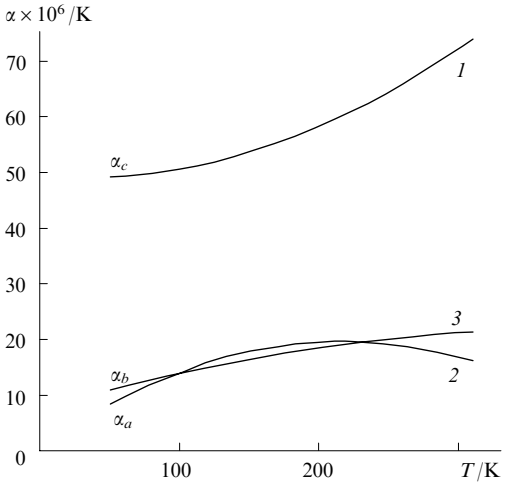


Figure 18. Temperature dependences of the thermal expansion coefficient for the (002) (*1*), (200) (*2*) and (060) (*3*) directions of an InI single crystal.[305]

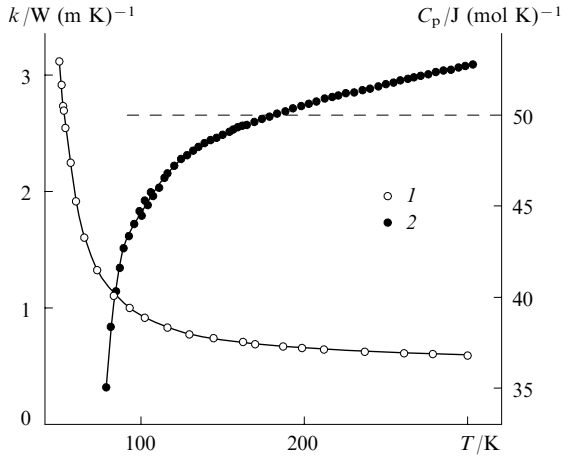


Figure 17. Temperature dependences of the thermal conductivity (*1*) and heat capacity (*2*) of an InI single crystal.[304] The theoretical value of the heat capacity is indicated by a dashed line.

A setup for the purification of InI powder by fractional distillation (Fig. 14) has been tested.[46] This setup was shown to be highly efficient for the purification from a number of impurities; the 99.999% purity was achieved. Single crystals were grown by the Bridgeman method in a quartz ampoule (Fig. 15).[304] The material is optically transparent to 50 μm (Fig. 16). Therefore, this is a promising material for far-IR optics. It is characterized by a very low thermal conductivity combined with a usual heat capacity (Fig. 17), as well as strong anisotropy in the thermal expansion (Fig. 18).[305]

VII. Conclusion

Polymorphism in indium iodides is still obscure and requires further investigation. It should be noted that extensive polymorphism and the existence of metastable modifications are typical of iodides of many metals.[307] The discrepancies between the published phase diagrams, results of research on the synthesis and structural data are necessary to address.

Many compounds that have been synthesized (*e.g.*, numerous InI_3 hydrates with other metal iodides) were not structurally characterized. It should be noted that the solution of the crystal structures provides the best way of determining the chemical composition of the compound.

A large number of new compounds, including indium monoiodide compounds with rare-earth metal iodides (which apparently play a substantial role in the operation of gas-discharge lamps), as well as of beryllium, calcium, zirconium and hafnium iodides are possible to synthesize.

Since indium triiodide is highly hygroscopic, its compounds are of little use for practical purposes as materials for IR optics. Most compounds with InI show incongruent melting behaviour and/or undergo polymorphic transformations, which interfere with the preparation of their single crystals from a melt. The compounds $InAlI_4$ and $InSn_2I_5$ are exceptions. Since aluminium iodide is highly hygroscopic, the former compound is of little interest, whereas indium iodostannate deserves special attention as a potential single-crystal medium (laser material for the IR range).

The characteristic coordination number of trivalent indium in iodides is 4 (coordination polyhedron is a tetrahedron). In this regard, its behaviour is similar to the behaviour of gallium in chlorides. The analogy is extended also to the formation of the complex anion $[In_2I_7]^-$ composed of two vertex-sharing tetrahedra. Meanwhile, the low-temperature modification of InI_3 is a rare example of the octahedral coordination of In^{3+}. This modification is characterized by a high density and, correspondingly, is stabilized under high pressure. Apparently, indium has the same coordination number in the dense modification of InI_2, too. It is of interest to elucidate the mechanisms of slow solid-state reactions and determine the factors responsible for the existence of a large number of metastable compounds. Probably, the slow kinetics of the synthesis is attributed to a change in the coordination number. It would be expected that at high pressure, the coordination number 6 will be usual for In^{3+} resulting in the total change in the crystal chemistry of indium iodide and the formation of entirely new compounds.

The behaviour of indium monoiodide, namely, the decomposition of the stable chemical compound in the presence of allegedly inert solvents, is of great interest.

An easy change in the valence of indium, which occurs with low potential barriers, facilitates the use of indium iodides as catalysts for various reactions of organic synthesis.

Complex compounds of indium may be employed for the development of new industrial processes. Continuing interest in organic compounds of indium (that are formed *in situ* or as intermediates) is confirmed by latest publications, for example, the studies,[308 – 316] which included investigations of the indium triiodide-catalyzed sulfidation of carboxylic acids with elemental sulfur to form symmetrical disulfides[313] and reduction of aromatic nitro compounds with tetramethyldisiloxane to amines,[316] as well as the formation of a carbon – carbon bond in the stereoselective reaction of alkenylindium diiodides with aryl(styryl) halides.[314]

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