GALLIUM AND GALLIUM COMPOUNDS

1. Introduction

Gallium (Ga)[7440-55-3], atomic number 31, was discovered through a study of its spectral properties in 1875 by P.E. Lecoq de Boisbaudan, a French chemist, and named from Gallia, the Latin name for France (also from Latin, gallus, a translation of Lecoq, a cock). Before its discovery, most of its properties had been predicted and described by Dmitri Mendeleev (who called the hypothetical element *eka-aluminium*) on the basis of its position in his periodic table. Later in 1875, Boisbaudran obtained the free metal through the electrolysis of its hydroxide in KOH solution. It was the first element to be discovered after the publication of Mendeleev's Periodic Table, its discovery constituted a confirmation of the Table which was reinforced shortly after by the discoveries of scandium (Sc) and germanium (Ge).

Gallium is a scarce but not a rare element. The concentration of gallium in the earth's crust is estimated at between 15–19 ppm compared with 16 ppm for lead and arsenic. Gallium is more abundant than antimony, silver, bismuth, molybdenum, and tungsten, however, it is present in very low concentrations, with little tendency to concentrate in a particular geologic environment. To date, ores containing gallium have not been economically mined solely for the contained gallium. Gallium is usually present in the 5–200 ppm range in most minerals. Some typical mineral analyses and rock averages are presented in Table 1 and 2. Gallium is generally concentrated in aluminum minerals (eg, bauxite, corundum). Gallium in rubies, the red gem variety of corundum, in some deposits in Tanzania and Malawi are between 10–500 ppm (1). They report

Table 1. **Gallium Abundances in Various Minerals**

Mineral	Formula	Ga ppm
Abite	$NaAlSi_3O_8$	40
Almandine	$Fe_3Al_2(SiO_4)_3$	20
Bauxite	$Al_2O_3\ 2H_2O$	90
Biotite	$K(Mg,Fe)_2AlSi_3O_{10}(OH)_2$	40
Calcite	$CaCO_3$	0.1
Chromite	$FeCr_2O_4$	18
Corundum	Al_2O_3	100
Cryolite	Na_2AlF_6	3
Diopside	$CaMg(SiO_3)_2$	5
Franklinite	$Zn(Fe,Mn)_2O_4$	10
Hematite	Fe_2O_3	1
Hornblende	$(Fe^{3+}, Fe^{2+},Al,Mg,Mn)_5(Ca,Na,K)_2Si_8O_{22}(OH)_2$	10
Jarosite	$KFe_3(SO4)_2(OH)_6$	8–23
Lepidolite	$KLiAl_2Si_3O_{10}(OH,F)_2$	100
Limonite	$2Fe_2O_3 \cdot 3H_2O$	3
Magnetite	$FeO\ Fe_2O_3$	30
Microcline	$KAlSi_2O_8$	40
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	200
Nepheline	$(Na,K)AlSiO_4$	20
Olivine	$(Mg,Fe)_2SiO_4$	2
Oligoclase	$(NaAlSi_3O_8)_{7-9}(CaAl_2Si_2O_8)_{3-1}$	10
Orthoclase	$KAlSi_3O_8$	10
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	50
Quartz	SiO_2	<1
Sodalite	$3NaAlSiO_4 \cdot NaCl$	100
Sphalerite	ZnS	1–1000
Spodumene	$LiAl(SiO_3)_2$	60

that gallium can be used with other trace elements to help distinguish rubies found in the "East African Trend" from other locations. Micas generally contain the most gallium of the rock-forming minerals; muscovite and phlogopite are usually richer than biotite. Feldspar contains more gallium than does pyroxene or olivine. Within the feldspar family, albite contains more gallium than does anorthite. The substitution of gallium by trivalent iron is demonstrated in magnetite and franklinite; however, hematite, goethite, and limonite formed by sedimentary or hydrothermal processes contain only trace gallium. Gallite, CuGaS2, from Namibia (South-West Africa) is the only known mineral that

Table 2. **Gallium in Rocks and Minerals**[a]

Material	Number of studies	Ga, ppm 10^4	Ga:Al
igneous rocks	323	22	3.3
metamorphic rocks	90	19	2.2
sedimentary rocks	166	16	2.8
bauxites	76	55	2.2
sphalerites	31	35[b]	

[a] Data are mean values.

[b] Observed to be quite variable, eq, 3–100 or more.

contains gallium as a primary constituent, but is considerably rare; the mineral germanite Cu3(Fe, Ge)S4 from Tsumeb, South-West Africa, has been found rich in gallium content (1.85%). The only other terrestrial sulfide mineral that contains significant gallium is sphalerite (Zn, FeS) with the concentration being temperature dependent; low-temperature specimens contain 100–1000 ppm Ga and high-temperature specimens contain <10 ppm Ga.

2. Abundance

Primary Ga ores are extremely rare, and Ga production from these sources has been very limited. Ga is primarily produced as a byproduct of Al extraction from bauxite ores that typically contain from 30 to 100 ppm Ga (see ALUMINUM AND ALUMINUM ALLOYS; ALUMINUM OXIDE (ALUMINA), ACTIVATED). Ga has many chemical similarities to Al but is much less abundant, with an average crustal abundance of 15–19 ppm (2,3). The chemical similarities between Ga and Al include a 3+ oxidation state, tetrahedral or octahedral coordination, amphotericity, and similar atomic radius. These properties account for the similar geochemical behavior of both elements.Ga is also recovered during Zn extraction from sulfide concentrates produced from Zn-rich polymetallic sulfide ores (see ZINC AND ZINC ALLOYS); these are the main sources of gallium. Gallium is found in the production of germanium from germanium minerals. In certain coals, the flue dust may contain 10–500 ppm Ga, sometimes as high as 10,000 ppm Ga (see COAL). Gallium has also been extracted from copper ores from the Apex Mine, St. George, Utah (4,5). The abundance of gallium in several common classes of rocks is shown in Figure 1.

2.1. Bauxite/Laterite Occurrence. Most gallium is recovered from bauxite developed over a wide variety of primary rocks weathered under tropical conditions. These rocks include, gneiss, diorite, pelitic schist, granite, basalt, andesite, and greywacke, among others. The limited mobility of Al as well as of Ga in near-surface environments account for Ga enrichment in bauxite and other ores derived from deeply weathered materials. For example, in many of the parent rocks, gallium is contained in feldspars substituting for aluminum. The early stage of weathering of primary host rocks is characterized by leaching of alkalis, alkali-earths and silicon, consequently, gallium and aluminum may remained linked in secondary minerals, typically kaolinite and gibbsite, retaining in part the originally affinity in the lateritic cover. However, this observed relationship is normally disturbed and eventually inverted when kaolinite and more prominently gibbsite are dissolved due to physico-chemical changes (6). The acid/base and electronic properties of Ga differ enough from those of Al that under certain geochemical conditions, these elements can be separated in near-surface environments by changes in pH or redox conditions. Gallium in hydrous species, commonly Ga-hydroxide, is more soluable then Al-hydroxide for pH values from 3 to 7 (7). Thus if early formed kaolinite and gibbsite are dissolved in acidic conditions, the resulting Ga- and Al hydroxides behave differently. Gallium may be leached to a greater extent than Al. Soluble Aluminum complexes are transferred to deeper zones in the lateritic crust or the upper

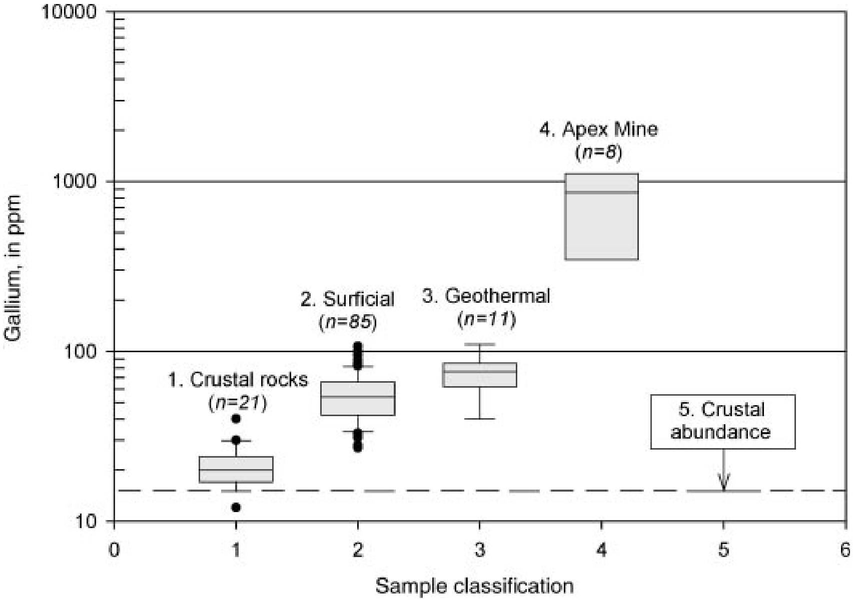

Fig. 1. Box plot of gallium abundance in designated rocks. The box contains the central 50 percent of the values where the upper box edge is for the 75th percentile and the lower box edge is for the 25th percentile. The line interior to the box is the median. The distance from the median to the 75th percentile is call the upper interquartile and the distance from the median down the 25th percentile edge is called the lower quartile. Whiskers occur at the 10th percentile below the box and at the 90th percentile above the box. The whiskers are capped with fences. Values outside the fences are possible outliers.

The classes are as follows:

1. Crustal rocks include observations from 21 samples and have Ga values between 12 and 40 ppm. The median value is 20 ppm.
2. Surficial includes observations from 85 samples that include Fe crusts, laterites, saprolites, and bauxite and have Ga values between 27 and 107 ppm. The median value is 54 ppm.
3. Geothermal observations are from 11 samples of crusts, etc. as found in geothermal deposits associated with active geothermal systems in New Zealand. Ga values are between 38 and 150 ppm and the median is 77 ppm.
4. Apex observations are from 8 samples found at the Apex Mine, Utah. Ga values range from 320 to 1,480 ppm and the median is 860 ppm.

part of the saprolite while gallium remains in solution and migrates out of the weathering profile. In these types of aluminum enriched horizons the Ga/Al ratio is relatively low. However, gallium is easily retained by Fe-Oxyhydroxides in ferruginous duricrusts and Fe-rich horizons of the bauxitic profiles yielding a distinct positive Ga vs. Fe correlation (6). Reported Ga concentrations between 27 and 107 ppm occur (Fig. 1) in surficial materials including samples from saprolites, Fe crusts, laterites, and bauxites.

2.2. Known Reserves. Assuming that the average content of gallium in bauxite is 50 parts per million (ppm), U.S. bauxite resources, which are mainly subeconomic deposits, contain approximately 15 million kilograms of gallium.

Table 3. **World Gallium Reserves and Reserve Base**[a]**, 10^6 kg**

	Reserves	Reserve base[b]
North America:		
United States	1	1
Other	49	49
Total	*50*	*50*
South America	92	99
Europe	16	17
Africa	86	93
Asia	50	57
Oceania	107	110
World total	*400*	*430*

[a] Modified from Ref. 3.

[b] The reserve base includes demonstrated resources that are currently economic(reserves), marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources).

About 2 million kilograms of this metal is present in the bauxite deposits in Arkansas. Some domestic zinc ores contain as much as 50 ppm gallium and, as such, could be a significant resource. World resources of gallium in bauxite are estimated to exceed 1 billion kilograms, and a considerable quantity could be present in world zinc reserves. The foregoing estimates apply to total gallium content; only a small percentage of this metal in bauxite and zinc ores is economically recoverable. Table 3 presents estimated world gallium reserves and reserve base (see Ref. 8 for definitions).

2.3. Speculative Resources. An early work documenting the occurrence of gallium in a geothermal system in Pleistocene and Recent volcanic rocks (9) reported that samples of muds from sinter flats at the Rotokawa Geothermal System have Ga concentrations between 35 and 120 ppm. Ga has a median of 77 ppm from eight sets of samples made of these muds plus two samples taken on the northeast margin of Lake Rotokawa. Recent geologic studies suggest hydrothermal system may contain even higher levels of Ga content. These studies have demonstrated Ga enrichment in zones of advanced argillic alteration associated with some hot-springs-type Hg deposits in Nevada (10). The inactive McDermitt Hg deposit in the Opalite mining district, Nev., has recently been evaluated as a potential source of Ga, and Ga contents as high as several hundred parts per million have been reported (11). Hot-spring-type Hg deposits are commonly associated with zones of advanced argillic alteration, suggesting that this alteration process may be responsible for the Ga enrichment (10). High Ga contents can occur in zones of advanced argillic alteration associated with several ore-deposit types, including hot-spring-type Hg, silica-carbonate Hg, hot-spring-type (low sulfidation) Au, and quartz-alunite (high sulfidation) Au-Ag deposits. The advanced-argillic-alteration assemblage typically consists of quartz, alunite, and kaolinite but, depending on the hydrothermal environment of formation, may include pyrophyllite, dickite, diaspore, zunyite, woodhouseite, rutile-anatase, and barite (12). In these deposits the highest Ga contents occur in the zones of advanced argillic alteration associated with quartz-alunite (high sulfidation) Au-Ag deposits, locally exceeding 100 ppm. The highest Ga contents are associated with the kaolinite-alunite-alteration assemblage. Very low Ga contents occur in quartz from the vuggy-silica-alteration core in such deposits as at the Ashgrove silica deposit, Wash. Low Ga contents occur in the zones of advanced argillic alteration associated with hot-spring-type Hg-Au deposits: generally less than 32 ppm. These large hydrothermal alteration zones are localized within volcanic centers where deposits of clay have been developed and mined. These zones host potentially significant resources of gallium either as a primary product or as a byproduct of clay extraction. This association may provide a model for other occurrences associated with other types of hydrothermal metallic deposits in the western United States, and may represent an important source of this metal that has not been widely recognized before.

Gallium is sometimes selectively mobilized and may result in gallium-enriched fluids. Rock analysis showed that gallium content in kyanite quartzite of the Piedmont Province of Central Virginia was greatly depleted (including samples from two economically important kyanite deposits) in many of the 23 samples collected from 9 locations (13). Researchers note that the Ga/Al ratio was very low and they hypothesis that the rocks were leached with acid hydrothermal fluids composed of H_2SO_4 and HF, as suggested by the presence of topaz.

3. Properties

3.1. Physical Properties.

Gallium, at. wt 69.717, has two stable isotopes, ^{69}Ga [14391-02-7], 60.4%, and ^{71}Ga [14391-03-8], 39.6%, and twelve unstable isotopes, from mass 63 through 76. The radius of the atom is 0.138 nm, and of the ions Ga^{3+} and Ga^{+}, is 0.062 nm and 0.133 nm, respectively. Solid gallium has a metallic, slightly bluish appearance.

The physical properties of gallium, especially its thermal properties, are exceptional (14). It has a low mp and vaporizes above 2200°C, ie, it has the longest liquid interval of all the elements. Also, it is easily supercooled. However, it expands during solidification by 3.2%, a property shared by only two other elements, germanium and bismuth. Its crystal structure is unusual for a metal. Gallium crystallizes in the orthorhombic system, and it is very anisotropic. This latter property is attributed to the existence of Ga−Ga covalent bonds along its [001] axis. Principal physical properties of the normal or alpha form are listed in Table 4. Only normal gallium (alpha or I) expands upon solidification. There are other isomorphic phases of gallium. Some, which are metastable at atmospheric pressure, are obtained from supercooled gallium. Some of the physical properties of the metastable forms are listed in Table 5.

Other forms of gallium are obtained at high pressure (15,16). The high pressure forms II, cubic, I-43d; and III, tetragonal, I4/mm; are formed at 2.8 GPa (280 kilobar) and 2.6 GPa (260 kilobar), respectively. The mp of the latter is 48.7°C.

Table 4. **Physical Properties of Normal Gallium**

Property	Value
melting point, °C	29.7714
boiling point, °C	ca 2200
density at mp, g/cm^3	
solid	5.904
liquid	6.095
heat of fusion, J/g[a]	79.8
heat capacity, J/(kg · K)[a]	
30°C	381.5
−17°C	361.4
−36°C	352.8
thermal conductivity, W/(m · K)	
solid at 20 °C	
a	88.4
b	16.0
c	40.8
liquid at 77°C	28.7
cubic coefficient of expansion, °C^{-1}	
solid at 0–20°C	5.95×10^{-5}
liquid	
at 103°C	1.20×10^{-4}
at 600°C	1.03×10^{-4}
vapor pressure, Pa[b]	
1198 K	0.14
1249 K	0.44
1321 K	1.74
1478 K	16.5
crystallographic properties	orthorhombic Cmca space group
a, nm	0.45186
b, nm	0.76602
c, nm	0.45258
z	8
electrical resistivity, μΩ · cm	
solid at 20°C	
a	8.1
b	54.3
c	17.4
polycrystal	15.05
liquid at 30°C	25.795
debye temperature, °C	51.6
viscocity, dynamic, mPa·s(=cP)	
32°C	1.810
50°C	1.739
surface tension, mN/m (=dyn/cm)	
30°C	709
400°C	733

[a] To convert J to cal, divide by 4.184.

[b] To convert Pa to mm Hg, divide by 133.3.

Gallium wets almost all surfaces, especially in the presence of oxygen which promotes formation of a gallium suboxide film. Gallium diffuses quickly into the crystal lattice of certain metals, particularly aluminum. If a line is traced with a piece of solid gallium on a sheet of aluminum, the aluminum quickly becomes

Table 5. **Physical Properties of Metastable Forms of Ga**[a]

	Metastable forms at normal pressure			
Property	β	λ	ε	γ
melting point, °C	−16.3	−19.4	−28.6	−35.6
heat of fusion, J/g[a]	38.0	37.0	36.2	34.9
density at melting point, g/cm^3	6.22	6.21		6.20
crystal structure	monoclinic	trigonal		orthorhombic
space group	C2/c	R$\bar{3}$m		Cmcm

[a] To convert J to cal, divide by 74.184.

brittle on that line as a result of the diffusion of gallium to the grain boundaries of the aluminum. Because of this property of embrittling aluminum, the DOT Office of Hazardous Materials has classified gallium in Hazard Class HM-181 and has placed restrictions on air shipment. IATA (international air transport regulation) classifies gallium as corrosive.

3.2. Chemical Properties. In accordance with its normal potential, gallium is chemically similar to zinc and is somewhat less reactive than aluminum. Just as aluminum, it is protected from air-oxidation at ambient temperature by a fine film of oxide. It is entirely oxidized by air and by pure oxygen at ca 1000°C. Normally, gallium is trivalent; however, it also may be monovalent. Gallium forms some compounds of mixed valence, eg, gallium (I) tetrachlorogallate(−1) [13498-12-9], $Ga(GaCl_4)$. Gallium slowly reacts with water below 100°C, but it is completely oxidized by water in an autoclave at 200°C. At ambient temperature, concentrated inorganic acids and gallium react slowly. Oxidizing agents, such as aqua regia, H_2SO_4, H_2O_2, and perchloric acid, attack gallium effectively, especially when hot. The halogens readily react with gallium upon heating, as do sulfur, selenium, tellurium, phosphorus, arsenic, and antimony. Nitrogen reacts with gallium only under particular conditions, whereas boron seems not to do so.

Amphoteric character is one of gallium's principal properties. Gallium oxide is more acidic than alumina, and thus solutions of gallates(III) are not as unstable as those of aluminates. Solutions of alkali hydroxides readily attack gallium at 100°C. In alkaline solutions, eg, of sodium gallate [12063-93-3], $NaGaO_2$, as in acidic solutions, eg, of $GaCl_3$, the solubility in terms of Ga can be very high, on the order of 1000 g/L of solution. At a temperature of 500-1000°C or more, gallium is very corrosive to most metals. Only tungsten is unaltered; niobium, tantalum, and molybdenum are less resistant.

4. Extraction

A minor amount of gallium is extracted as a by-product from the zinc industry. The gallium content of sphalerites generally is concentrated in the residues of zinc distillation and in the iron mud resulting from purification of zinc sulfate solutions. Gallium is extracted from these streams by acidic solutions and gallium salts are recovered by liquid-liquid extraction using dialkylphosphates, trialkyl phosphates, hydroxyquinolines, or isopropyl ether, among others (see EXTRACTION, LIQUID–LIQUID) (17).

4.1. Recovery from Bayer Liquor.

The significant amount of primary gallium is recovered from the alumina industry. The main source is the sodium aluminate liquor from Bayer-process plants that produce large quantities of alumina. Several methods have been developed to recover gallium from Bayer liquor.

Carbonation. Gallium can be extracted by fractional carbonation which consists of treating the aluminate solution with carbon dioxide in several controlled stages. This process is no longer under industrial operation (18).

Electrolysis. Gallium can be extracted by direct electrolysis of the aluminate solution at a strongly agitated mercury cathode. The recovery from a sodium gallate solution resulting from the carbonation process is another possibility. This process is probably no longer operative because of the environmental problems associated with the mercury.

Chemical Reduction. Reduction of gallium by aluminum has been developed in the former Soviet Union. This method is in operation. The Bayer liquor is contacted using a gallium–aluminum alloy named Gallam, and the gallium is deposited.

Liquid–Liquid Extraction. Among the various extractants available for the recovery of metals from aqueous streams, only 8-hydroxyquinoline derivatives are effective for the recovery of gallium from Bayer liquor. A process has been developed and patented (19–24). Production began in 1980 in Salindres, France, followed in 1989 in Pinjarra, western Australia.

Ion-Exchange Resins. Some attempts have been carried out to recover gallium by ion exchange (qv). Only the commercially available amidoxime resin has proved to be effective for the recovery of gallium from Bayer liquor. The process has been developed and patented (25) and is reported to be under operation in Japan.

4.2. Purification.

Extraction from aluminum or zinc ores produces crude gallium metal or concentrates. These concentrates are transformed to sodium gallate, gallium chloride, or gallium sulfate solutions which are purified, then electrolyzed. Gallium is deposited as a liquid.

The purification of the gallium salt solutions is carried out by solvent extraction and/or by ion exchange. The most effective extractants are dialkyl-phosphates in sulfate medium and ethers, ketones (qv), alcohols, and trialkyl-phosphates in chloride medium. Electrorefining, ie, anodic dissolution and simultaneous cathodic deposition, is also used to purify metallic gallium.

Ultrahigh Purity Gallium. Many applications, particularly those in the electronics industry (see ELECTRONIC MATERIALS), require high ($>$99.99999% = 7.N) purity metallic gallium. This is achieved by a combination of several operations such as filtration, electrochemical refining, heating under vacuum, and/or fractional crystallization (see ULTRAPURE MATERIALSED) (26).

Recycling. A large part of the wastes from the gallium arsenide [12064-03-8], GaAs, industry is recovered for both economical and environmental reasons. Several processes are effective and being used to recover both the gallium either as a metal, a salt, or a hydroxide for recycling, and the arsenic in some form for recycling or disposal. Thermal decomposition of gallium arsenide waste is one method which competes with the use of hydrometallurgical routes in caustic soda media (see RECYCLING, NONFERROUS METALS).

5. Production

Estimated crude gallium production was 70 metric tons (t) in 2003. Principal world producers were China, Germany, Japan, and Russia. Gallium also was recovered in Hungary, Kazakhstan, Slovakia, and Ukraine. Refined gallium production was estimated to be about 98 t; this included some new scrap refining. China was a significant source of crude gallium after 2000, supplying 84% of U.S. imports and an estimated 22% of Japan's imports. France was the largest producer of refined gallium using gallium produced in Germany as feed material. Japan and the United States also refined gallium. Gallium was recycled from new scrap in Germany, Japan, the United Kingdom, and the United States.

Gallium production in industrialized nations often reflects a complex array of internal and external sources. For example, in 2001, Japan's virgin gallium production was reported at 8 t, gallium recovered from scrap was cited at 50.2 t, and gallium imports were reported to be 67 t, for a total supply of 125 t. Total demand for gallium in Japan was estimated to be 96 t. The principal source countries for Japan's gallium imports were the United States (21.5 t), Kazakhstan (11.1 t), China (10.9 t), and France (9.7 t). In 2002, production was estimated to have remained at 8 t, with imports dipping to 44.5 t, and scrap recovery increasing to 44 t. Gallium demand in Japan was projected to increase to 114 t.

The gallium either comes from mining sources or is recycled from scrap. Scrap-recycling capacity is taking a larger place each year and in 1992 represented about 30 t. In the United States, the main producers of gallium are Gallium Compounds LLC, formerly Eagle-Picher Technologies, and Recapture Metals. Gallium Compounds LLC produces high-purity gallium trichloride and gallium metal, but will not recover gallium from GaAs or other scrap material (27). Consequently, Recapture Metals, Inc in Blanding UT, is the only gallium reprocessor in the United States. The company recovers gallium from scrap materials predominantly those generated during the production of GaAs and have the capacity to produce about 40 metric tones per year of the metal. Companies that reprocess gallium in Japan include Rasa Industries, Mitsubishi Metals, and Sumitomo Metal Mining; in France, Rhône-Poulenc; and in Germany, Preussag (Metaleurop) and Ingal.

5.1. Foreign Trade. In 2003, U.S. gallium imports were higher than those in 2002 but had not reached the levels of the previous 10 years. China (39%), Ukraine (19%), and Russia (13%) were the leading sources of imported gallium. U.S. consumption of gallium metal has diminished mainly because a significant portion of the GaAs manufacturing capacity has moved to other countries, such as China and Taiwan. Gallium metal consumption, therefore, is not expected to be as large as it has been in the past several years.

In addition to gallium metal, GaAs wafers were imported into the United States (see Table 6). In 2003, 15,400 kilograms (kg) of undoped GaAs wafers and 127,000 kg of doped GaAs wafers were imported. Japan was the leading

Table 6. **U.S. Imports for Consumption of Gallium Arsenide Wafers, by Country**[a]

	Gallium arsenide wafers, undoped				Gallium arsenide wafer, doped			
	2002		2003		2002		2003	
Country	Quantity (kilograms)	Value[b]	Quantity (kilograms)	Value[b]	Quantity (kilograms)	Value[b]	Quantity (kilograms)	Value[b]
China	15	$11,300	15	$9,450	759	1,140,000	24,800	23,500,000
Finland					12,000	20,000,000	11,200	12,700,000
France			1	18,000	6,060	15,200,000	4,440	9,790,000
Germany	211	31,400			18,900	14,700,000	22,200	22,700,000
Italy					14,900	154,000	80	15,800
Japan	7,830	201,000	14,000	341,000	49,500	30,800,000	36,700	30,900,000
Korea, Republic of	9	9,750			335	336,000	14,500	6,930,000
Taiwan			36	167,000	7,410	5,600,000	8,980	8,390,000
United Kingdom	47	101,000	1,320	26,500	467	774,000	1,600	304,000
Other	53	61,600	107	244,000	1,980	4,910,000	2,890	1,880,000
Total	*8,160*	*416,000*	*15,400*	*806,000*	*112,000*	*93,500,000*	*127,000*	*117,000,000*

[a] Data are rounded to no more than three significant digits; may not add to totals shown.

[b] Customs value.

Source: U.S. Census Bureau.

source of both types of wafers. The data listed in table 4 may include some packaging material and, as a result, may be higher than the actual total weight of imported wafers.

6. Economic Aspects

A report from Communications Industry Researchers Inc. predicted that the global LED market would grow to \$5.6 billion in 2008 from \$3.2 billion in 2004. According to the report, by 2008 the HB-LED market will be worth \$2.64 billion, while ultrahigh-brightness LEDs will have gained a 22% share of the global LED market. Rapid cost reduction is expected to begin in 2004, which would allow unit volumes to increase rapidly. Standard and indicator LEDs will make up the bulk of shipments initially, but HB-LEDs and ultrahigh-brightness LEDs will account for a significant majority of the revenues by 2008. Automotive, backlighting, and signage applications will compose more than 60% of the market during the 2004–08 period. In a separate report from Strategies Unlimited (a research unit of PennWell Corp.), the market for HB-LEDs grew by 47% in 2003 to reach \$2.7 billion, and the HB-LED market has grown by 350% since 1995, which represents a compound annual growth rate of 47%. Mobile appliances accounted for 50% of the HB-LED market in 2003. Signage was the next largest segment with 18%, followed by automotive applications at 15%, and illumination with 5%. All these segments enjoyed solid growth, with a minimum 21% market increase in 2003. The company expected the mobile market to start leveling out, reducing overall market growth to 17% from 2004 to 2008 (28).

According to a report by Strategies Unlimited, the market for GaN devices (primarily blue, green, and white high-brightness LEDs) has grown by 221% to \$1.35 billion since 1999. The company predicted that the market for GaN devices of all types would grow to \$4.5 billion by 2007. Since the beginning of the first significant commercial shipments of GaN LEDs in 1995, the market has grown at an average annual rate of 64.5%. Shipments of blue-violet laser diodes based on GaN devices began in 1999 and grew moderately through 2002. However, in 2003, a new market for blue-violet (405-nm) laser diodes in optical storage opened, as several companies announced the first shipments of the next generation of high-density DVD recorders. GaN-base electronic devices are still under development, but the first significant commercial shipments are expected to begin in 2004 (29).

A report from Strategy Analytics predicted that the GaN laser diode market would reach \$272 million by 2008 compared with \$9 million in 2003, which would be a compound annual growth rate of 195%. Although established markets for GaN lasers currently include biological agent detection, laser projectors, printing, and spectroscopy, the emergence of blue-violet-laser-based DVD recorders and increased demand for HDTVs were expected to boost GaN laser diode consumption. Strategy Analytics projected that blue-violet DVD applications would account for 97% of the total market by 2008. Currently, the market is much more divided, with 43% of sales listed under other applications, which include biodetection, machine vision, metrology, microlithography, projection displays, and underwater communication. In order for this to happen, the blue-violet

DVD platform needs to be standardized. The existence of two competing standards for blue-violet DVD—Blu-ray and high-density—will mean that the GaN laser diode market will still be at an early stage of development in 2008 (30).

Despite very strong growth in the market for many gallium-containing devices used in electronics, achieving a balance in the gallium industry has been difficult economically. Because of a significant over-capacity in the gallium industry, prices have been weak and are decreasing. Light-emitting diodes (LED) must face increasing competition from liquid crystal displays (LCD) and other alternatives to cathode ray tubes (CRT) for display devices. However, developments in LED technology have created a new market in large area outdoor and semi-outdoor displays. In Japan, high brightness GaAlAs LEDs are used as rear braking lights in automobiles.

Gallium-based laser diodes have also lost some of the market in telecommunications to indium-based devices. Optical fiber systems moved to the use of longer wavelengths for long distance networks.

Nevertheless, the market in compact disc equipment is increasing, and computer data storage has expanded rapidly, as well as telecommunication by satellite and the use of high frequency devices.

In spite of the limited growth of gallium demand, the forecast for use in integrated circuits (qv) shows an increasing market. Vitesse Semiconductor, in the United States, announced the very large-scale integration (VLSI) products based on GaAs which should compete with emitter coupled logic (ECL) devices. Also in the United States, Gigabit Logic and Gazelle Microcircuits are marketing devices which can readily replace silicon-based products. The high speed of GaAs is a great advantage in the military, space and supercomputing, and general computer markets.

Another attractive application for gallium is the use in high performance photovoltaic cells (qv) in satellites, but owing to the weight of the substrates, these have been replaced by germanium. The solar cells are manufactured using multiple layers of gallium compounds deposited by metalloorganic chemical vapor deposition (MOCVD) on the Ge substrates.

Gallium prices, stable up to 1991, fluctuated in 1992 because of gallium from China and Eastern European Bloc countries. The market destablized owing to spot offers and dumping. The reliability of these products was a real problem, however, and the consequence of market variations was dramatic for small manufacturers.

7. Analytical Methods

Gallium is easily identified spectrographically, eg, using the lines 287–294 and 403–417 nm. It is somewhat difficult to separate from aluminum and zinc by chemical means. The best method is the extraction of gallium chloride in acidic medium using an organic solvent, eg, diethyl or diisopropyl ether. Gallium can also be identified by colorimetry (using rhodamine B), fluorometry (using 8-hydroxyquinoline), gravimetrically (using 5,7-dibromo-8-hydroxyquinoline), or by complexometry and titration (EDTA).

The conventional method for quantitative analysis of gallium in aqueous media is atomic absorption spectroscopy (qv). High purity metallic gallium is characterized by trace impurity analysis using spark source (31) or glow discharge mass spectrometry (qv) (32).

8. Health and Safety Factors

Elemental Ga is insoluble in water and is therefore poorly absorbed in mammals. Inorganic salts of Ga (eg, gallium oxide, gallium trichloride, etc) undergo hydrolysis of hydroxide, which is also insoluble, and become colloidal in biological tissues (33). Severe intravenous overexposures are lethal because of kidney failure. Renal damage was similar to that seen for mercury.

Very little toxicological data is available on Ga effects in humans. Experiments in general, on the Ga-containing drugs have shown that anorexia, nausea, vomiting, skin rashes, and depression of red and white blood cell counts can occur. Other clinical experiments on Ga-containing drugs have resulted in some bone marrow depression, dermatitis and severe itching and gastrointestinal disturbances.

The toxicity of metallic gallium or gallium salts is very low. The corrosive, poisonous, or irritating nature of some gallium compounds is attributable to the anions or radicals with which it is associated. Gallium metal-organics, such as $Ga(CH_3)_3$, react vigorously with air, and can be explosive. The gallium halides, except the fluoride, hydrolyze in water to form corresponding halogen acids. Gallium phosphide, arsenide, selenide, and telluride react slowly with water, and more vigorously with acids and bases, to liberate toxic compounds. The LD_{50} of the solution of [$Ga(NO_3)_3 \cdot 9H_2O$] for mice is ca 3–4 g/kg. The ^{72}Ga and ^{67}Ga isotopes were studied, eg, as citrate salts, for detection of tumors. ^{72}Ga concentrates in bone tissues and ^{67}Ga seem to have a tumor-specific affinity. Additional data are available (33,34).

Gallium arsenide (GaAs), a group IIIa–Va intermetallic semiconductor, was nominated for a recent study because of its widespread current use in the microelectronics industry, the potential for worker exposure, and the absence of chronic toxicity data. Processing of GaAs wafers produces fine particulate crystals, which may present a hazard to industrial workers (35). Previous toxicological studies in animals and culture caused both the Environmental Protection Agency and World Health Organization to classify GaAs as an immunotoxicant and potential carcinogen (36,37).

Exposure of mice to GaAs, through intratracheal instillation or intraperitoneal administration, causes systemic inhibition of immune function (38). Immunosuppression in these cases is linked to faulty activation of helper T cells (39,40). Although health risks to industrial workers exposed to GaAs remains unclear, animal studies have established that chemical exposure causes detrimental biological effects. Intratracheal instillation and inhalation of GaAs results in pulmonary inflammation and edema in rodents (41–44). Tissue damage is associated with accumulation of neutrophils and macrophages. In contrast to systemic immune defects, GaAs has the opposite effect at the exposure site. A single intratracheal dose of GaAs or chronic inhalation in rodents results in pulmonary edema, fibrosis, and pneumocyte hyperplasia with accompanying accumulation of macrophages and neutrophils (63–65). Hence, the ability of GaAs to up-regulate proinflammatory cytokines may extend to the lungs, which could contribute to pulmonary damage.

The testicular toxicities of two compound semiconductor materials, gallium arsenide (GaAs) and indium arsenide (InAs), and arsenic oxide (As_2O_3) were also examined in rats (45). A significant decrease in sperm count and significant increase in the proportion of morphologically abnormal sperm were found in the epididymis in the GaAs group. It seems likely that, along with arsenic, gallium and indium play a role in the testicular toxicities of GaAs and InAs.

9. Uses

More than 95% of the gallium consumed in the United States was in the form of GaAs. GaAs was manufactured into optoelectronic devices (LEDs, laser diodes, photodetectors, and solar cells) and integrated circuits (ICs). ICs and optoelectronic devices each accounted for 41% of domestic consumption, 18% was used in research and development, and less than 1% was used in other applications (Table 7, (46)).

9.1. Gallium Using Epitaxial Technologies. *Diodes.* Most light-emitting diodes (LEDs) use vapor-phase epitaxy (VPE) or liquid-phase epitaxy (LPE) to grow GaAs, GaAsP, or GaP layers (47–50). The superbright red LED uses LPE to grow AlGaAs on GaAs or AlGaAs substrates. Epitaxial growth based on MOCVD technology is used in manufacturing some types of infrared LEDs used as optocouplers. MOCVD is also used to grow a GaAlAs or a GaAs layer (Buffer layer) on GaAs substrates for low cost optic fibers dedicated to local area networks (51) (see FIBER OPTICS; LIGHT-EMITTING DIODES).

GaAs, GaAlAs, and GaP based laser diodes are manufactured using the LPE, MOCVD, and molecular beam epitaxy (MBE) technologies (52). The short wavelength devices are used for compact disc (CD) players, whereas the long wavelength devices, mostly processed by MBE, are used in the communication field and in quantum well structures.

Table 7. **U.S. Consumption of Gallium, by End Use**[a,b,c]

End use	2002	2003
optoelectronic devices:		
laser diodes and light-emitting diodes	7,430	7,630
photodetectors and solar cells	386	524
integrated circuits:		
analog	8,600	8,090
digital	560	51
research and development	1,630	3,720
other	10	94
Total	*18,600*	*20,100*

[a] Ref. 46.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Includes gallium metal and gallium compounds.

Transitor Amplifiers. Most gallium-based field-effect transitor amplifiers (FETs) are manufactured using ion implantation (qv) (53), except for high microwave frequencies and low noise requirements where epitaxy is used. The majority of discrete high electron mobility transistor (HEMT) low noise amplifiers are currently produced on MBE substrates. Discrete high barrier transistor (HBT) power amplifiers use MOCVD and MBE technologies.

Integrated Circuits. For analogue integrated circuits (ICs) as frequencies increase, requirements for epitaxy grow at the same rate. For most microwave devices with frequencies over 20 GHz, an epitaxial GaAs layer is required. MBE is preferred for HEMT structures with better low noise, while MOCVD is used for HBT devices (see INTEGRATED CIRCUITS).

Photovoltaics. Photovoltaic applications require GaAs wafers and epitaxial layers. In most applications of photovoltaics in space, germanium substrates with GaAs active layers are used. Night vision system (NVS) devices use an epitaxial layer of GaAs applied to one end of a photomultiplier to enhance infrared images. The epitaxial layer consists of a 5 to 50 μm layer grown on a GaAs substrate using MOCVD techniques.

Other Applications. Recently, the industry's first single-crystal 2-inch GaN wafers were shipped to a major device manufacturer. The single-crystal GaN substrates are 500 μm thick and have greater than 90% usable area for circuit fabrication. The 2-inch diameter substrates are N-type and may be used as base raw material for a variey of applications in communications and semiconductor products, covering a range of systems from optical storage to wireless handsets to radar (54).

Lasers (qv) having wavelengths between 690 and 900 nm utilize GaAlAs. Main applications are fiber optic communication, digital audio disk, video disk, laser printer, optical recording, and test and measurement instruments. When using InGaAsP the wavelength changes from 0.7 μm up to 1.5 μm.

In photodetectors (qv) for photocouplers, optical switches, fiber optics, communication, and imaging, the materials used are InGaAs, InGaAsP, and GaSb.

Materials used in optical ICs are GaAs, InSb (for optoelectronic ICs), GaAlAs, InGaAsP (for optical array), and GaAlAs. Main applications are in supercomputers, design for very large-scale integration (VLSI) circuitry, nuclear fusion control, research of resources, high speed data system, control memories for large computers, memories for large-scale integration (LSI) testers, and direct broadcasting satellite receivers.

High voltage power transistors having high (<ns) speed switching, very high (200 V) blocking voltage, working voltage of 1000 V, and a total current 10 times higher than Si MOSFET and twice as high as Si bipolar, use gallium. The materials used in magnetoelectric transducers are InSb, GaAs, and InAs. Applications are precision motors, direct drive motors, tension controllers (tape disk, disk deck, microcomputers), tape end sensors, and microcomputer-controlled machinery.

Magnet Applications. For magnets of the type FeNdB, a small amount of gallium is effective in improving the intrinsic coercive force (55). It slows the pinning type recoil loop. The thermal stability is increased. The irreversible loss is less than 1.5% under 373 K (1000 h).

9.2. Medical Uses of Gallium. Gallium can be used to detect such diseases as Hodgkin's disease, lymphomas, and interstitial lung disease (56). Gallium nitrate is also used as an anticancer drug for lymphomas and bones (57). It can reverse bone degeneration and/or hypercalcemia cancer, osteoporosis, and Paget's syndrome. In the case of therapeutic action gallium halts bone resorption, normalizes serum calcium levels, adds bone mass, and kills cancer cells. Some gallium drugs become acute renal toxins at 10 to 100 times the therapeutical dose. Gallium does not accumulate in tissues, nor does it cause mutations or show other signs of toxicity.

In dental applications gallium alloys are nonstaining and used in the fabrication and repair of dental protheses. These alloys exhibit a sufficiently high solder temperature enabling presoldering of the alloy without distortion of the restoration (58) (see DENTAL MATERIALS).

9.3. Catalysis Application. Gallium is used in catalysts for aromatization in the petroleum (qv) industry (59). Benzene, toluene, and xylene can be produced by oligomerization and cyclization using zeolites containing 1 to 4% gallium as gallium nitrate (see BTX PROCESSING; MOLECULAR SIEVES). A gallium 99.999% is used and from 5 to 8 t/yr was forecasted for this application in 1993.

10. Alloys And Intermetallic Compounds

10.1. Alloys. Gallium has complete miscibility in the liquid state with aluminum, indium, tin, and zinc. No compounds are formed. However, these binary systems form simple eutectics having the following properties:

Metal	Ga, %	Melting point, °C
Al	96	26.4
In	76	15.7
Sn	91.5	20.6
Zn	96.3	25.0

The systems obtained when gallium is in the presence of bismuth, cadmium, germanium, mercury, lead, silicon, or thallium present miscibility gaps. No intermetallic compounds are formed.

10.2. Intermetallic Compounds. Numerous intermetallic gallium-transition element compounds have been reported (60). The principal compounds are listed in Table 8 (61–66). There are probably several Cs and Rb compounds; however, none is well known.

10.3. Lanthanides and Yttrium. The following compounds are known: MGa_2, hexagonal (M=Dy, La, Nd, Sm and Tb); MGa, orthorhombic; M_5Ga_3, tetragonal; MGa_2, hexagonal (M=Eu and Yb); MGa_3, cubic (M=Lu, Tm); MGa, orthorhombic; M_5Ga_3, hexagonal; $ErGa_3$ [12785-97-6], cubic; $ErGa_2$ [60874-25-1], hexagonal; Er_5Ga_3 [12324-45-7], hexagonal; $GdGa_2$ [12690-00-5], hexagonal; GdGa [12310-95-1], orthorhombic; Gd_3Ga_2 [12683-05-5], tetragonal; Gd_5Ga_3

Table 8. **Intermetallic Compounds**

Compound	CAS Registry number	Crystal form	Compound	CAS Registry number	Crystal form
Ag_3Ga	[57673-45-7]	hexagonal	$NbGa_3$	[12160-73-5]	tetragonal
AgGa	[12260-08-1]	hexagonal	Nb_5Ga_{13}	[12160-83-7]	orthorhombic
$AgGa_2$	[12044-77-8]	cubic	Nb_5Ga_4	[12024-35-0]	hexagonal
AuGa	[12006-53-0]	orthorhombic	Nb_3Ga_2	[12306-31-9]	trigonal
Au_2Ga	[54327-67-2]	orthorhombic	Nb_5Ga_3	[12024-30-5]	trigonal
Au_7Ga_2	[12536-48-6]	hexagonal	Nb_3Ga	[12024-05-4]	cubic
$BaGa_4$	[12230-66-9]	tetragonal	$NiGa_4$	[56627-21-5]	cubic
$BaGa_2$	[12258-56-9].	hexagonal	Ni_2Ga_3	[12629-62-8]	tetragonal
BaGa	[12258-55-8]	hexagonal	Ni_3Ga_4	[12435-24-4]	cubic
Ba_3Ga_2	[12258-59-2]	trigonal	$Ni_{13}Ga_9$	[12500-13-9]	monoclinic
Be_3Ga	[73156-95-3]		Ni_3Ga_2	[56541-04-8]	hexagonal
CaGa4	[12177-60-5]	tetragonal	Ni_5Ga_3	[12401-05-7]	orthorhombic
$CaGa_2$	[12258-68-3]	hexagonal	Ni_3Ga	[12063-96-6]	cubic
CaGa	[12258-67-2]	orthorhombic	O_5Ga_3	[60862-21-7]	tetragonal
$CeGa_2$	[12157-58-3]	hexagonal	$PdGa_5$	[52935-27-0]	tetragonal
CeGa	[20328-37-4]	orthorhombic	Pd_3Ga_7	[73157-02-5]	cubic
$CeGa_3$	[12360-78-0]	tetragonal	PdGa	[59125-32-5]	cubic
Ce_5Ga_3	[12360-78-0]	tetragonal	Pd_5Ga_4	[73157-03-6]	cubic
Ce_3Ga	[73623-49-1]	cubic	Pd_5Ga_3	[52935-26-9]	orthorhombic
$CuGa_2$	[12443-57-1]	tetragonal	Pd_5Ga_2	[53095-62-8]	orthorhombic
CuGa	[12191-11-6]		Pd_2Ga	[12529-00-9]	orthorhombic
Cu_2Ga	[69847-96-7]	cubic	$PtGa_6$	[12411-32-4]	orthorhombic
Cu_9G_4	[12395-15-2]	cubic	Pt_3Ga_7	[12411-33-5]	cubic
Cu_3Ga	[68985-62-6]	cubic	$PtGa_2$	[12786-51-5]	cubic
$FeGa_2$	[12062-72-5]	tetragonal	Pt_2Ga_3	[12411-26-6]	tetragonal
Fe_3Ga4	[53237-41-5]	monoclinic	PtGa	[12411-22-2]	cubic
FeGa	[71771-30-7]	cubic	Pt_5Ga_3	[12411-27-2]	orthorhombic
Fe_6Ga_5	[53262-40-1]	monoclinic	Pt_2Ga	[12401-01-3]	cubic
Fe_2Ga	[12160-14-4]	hexagonal	Pt_3Ga	[12411-23-3]	cubic
Fe_3Ga	[12063-30-8]	cubic	Rh_2Ga_9	[66703-44-4]	monoclinic
$HfGa_3$	[73156-96-4]	tetragonal	$RhGa_3$	[60862-22-8]	tetragonal
$HfGa_2$	[12186-72-0]	tetragonal	$Rh_{10}Ga_{17}$	[12064-38-9]	tetragonal
Hf_2Ga_3	[73156-97-5]	orthorhombic	RhGa	[73157-04-7]	cubic
Hf_5Ga_3	[73156-98-6]	hexagonal	$RuGa_3$	[60862-23-9]	tetragonal
Hf_2Ga	[12786-47-9]	tetragonal	$RuGa_2$	[12064-21-0]	orthorhombic
$IrGa_3$	[60682-20-6]	tetragonal	RuGa	[39388-93-7]	cubic
Ir_3Ga_5	[12064-32-3]	tetragonal	$SrGa_4$	[12160-78-0]	tetragonal
IrGa	[60921-95-1]	cubic	$SrGa_2$	[12259-26-6]	hexagonal
KGa_4	[12435-22-2]	orthorhombic	Sr_3Ga_2	[12259-27-7]	cubic
K_5Ga_8	[73156-99-7]		Ta_3Ga_2	[60862-19-3]	tetragonal
LiGa	[12519-03-8]	cubic	Ta_5Ga_3	[12160-75-7]	tetragonal
Li_3Ga_2	[63705-92-0]		$TiGa_3$	[12064-30-1]	tetragonal
Li_2Ga	[39343-49-2]		$TiGa_2$	[12186-73-1]	tetragonal
$LiGa_2$	[39343-50-5]		TiGa	[12398-41-3]	tetragonal
$LiGa_3$	[53570-25-5]		Ti_5Ga_4	[65453-84-1]	hexagonal
Mg_2Ga_5	[12411-31-3]	tetragonal	Ti_5Ga_3	[68565-51-5]	tetragonal
$MgGa_2$	[12411-25-5]	orthorhombic	Ti_2Ga	[12500-08-2]	hexagonal
MgGa	[12063-92-2]	tetragonal	Ti_3Ga	[12183-38-9]	hexagonal
Mg_2Ga	[12422-88-7]	hexagonal	V_8Ga_{41}	[55071-08-4]	tetragonal
Mg_5Ga_2	[12064-14-1]	orthorhombic	V_2Ga_5	[12024-48-5]	tetragonal
$MnGa_4$	[12160-76-8]	cubic	V_6Ga_7	[12024-50-9]	cubic
Mn_2Ga_5	[12763-96-1]	tetragonal	V_6Ga_5	[12024-49-6]	tetragonal

Table 8 (*Continued*)

Compound	CAS Registry number	Crystal form	Compound	CAS Registry number	Crystal form
Mn_7Ga_6	[73157-00-3]	tetragonal	V_3Ga	[12024-15-6]	cubic
Mn_3Ga_2	[12160-70-2]	tetragonal	$ZrGa_3$	[12064-31-2]	tetragonal
Mn_8Ga_5	[73157-01-4]	cubic	$ZrGa_2$	[112186-74-2]	
Mn_2Ga	[12160-55-3]	hexagonal	Zr_3Ga_5	[73156-91-9]	
Mn_3Ga	[12186-69-5]	hexagonal	Zr_2Ga_3	[73156-92-0]	
Mo_8Ga_{41}	[55071-07-3]	tetragonal	ZrGa	[73156-93-1]	tetragonal
Mo_6Ga_{31}	[52015-37-9]	monoclinic	Zr_5Ga_4	[73156-94-2]	hexagonal
Mo_3Ga	[37381-83-2]	cubic	Zr_3Ga_2	[66703-42-2]	tetragonal
$NaGa_4$	[12435-23-2]	tetragonal	Zr_5Ga_3	[66103-56-8]	hexagonal
Na_5Ga_8	[39297-66-0]		Zr_2Ga	[12786-50-4]	tetragonal

[12324-83-3], tetragonal; $HoGa_3$ [67352-19-6], cubic; $HoGa_2$ [12599-74-5], hexagonal; HoGa [12310-96-2], orthorhombic; Ho_5Ga_3 [12324-84-4], hexagonal; $PrGa_2$ [12599-76-7], hexagonal; PrGa [12310-99-5], orthorhombic; Pr_5Ga_3 [12361-85-2], orthorhombic; YGa_2 [12435-21-1], hexagonal; YGa [12160-65-5], orthorhombic; and Y_5Ga_3 [12024-34-9], hexagonal.

10.4. Actinides. The following compounds are known: U_2Ga_3 [37381-84-3], orthorhombic; UGa_2 [12064-23-2], hexagonal; UGa_3 [12024-33-8], cubic (67); $PuGa_6$ [12160-80-4], tetragonal; $PuGa_4$ [12160-77-9], orthorhombic; $PuGa_3$ [12024-31-6], hexagonal; $PuGa_2$ [12160-71-3], hexagonal; PuGa [12160-58-6], tetragonal; Pu_5Ga_3 [12160-74-6], tetragonal; and Pu_3Ga [12160-59-7], tetragonal. Gallium is also used at low (ca 1%) concentrations to stabilize the delta phase of plutonium.

11. Compounds Other Than Intermetallic

Gallium compounds containing monovalent elements are described in Reference (68).

11.1. Hydrides. Gallium(I) hydride [13572-92-4], GaH, is detected only in the vapor phase. The hydride of Ga(III), gallane [13572-93-5], GaH_3, which decomposes above −15°C, can be obtained by reaction of trimethylaminegallane [19528-13-3], $(CH_3)_3N \cdot GaH_3$, and boron fluoride, BF_3, at −20°C. Halogen derivatives of gallane, especially dichlorogallane [13886-65-2], $GaHCl_2$, and dibromogallane [13886-66-3], $GaHBr_2$, are obtained by reaction of trimethylsilane and $GaCl_3$ or $GaBr_3$, respectively, below −20°C. The colorless crystals of dichlorogallane are stable up to 29°C. The dibromogallane decomposes at −5°C.

Mixed hydrides, $MGaH_4$, where M= Li, [17836-90-7]; Na, [32106-51-7]; K, [32106-52-8]; Rb [32104-62-4]; and Cs [32104-63-4] also are known. The lithium gallium hydride [17836-90-7], is the most stable, and has been studied as a reagent for organic reactions. It is similar to the aluminum compound, $LiAlH_4$.

A number of organic derivatives of gallane, both addition and substitution compounds, are known. Some are much more stable than gallane, eg, $(CH_3)_3N \cdot GaH_3$, $(CH_3)_3P \cdot GaH_3$ [15279-03-5], and $(CH_3)_2N \cdot GaH_2$ [32342-80-6]. These are used for the preparation of other organic compounds of gallium.

Table 9. **Properties of Gallium Halides**[a]

Compound	CAS Registry number	Mp °C	Density, g/cm^3	Crystal structure	Space group
$GaFe_3$	[7783-51-9]	subl. 800	4.47	trigonal	$R\bar{3}c$
$Ga(GaCl_4)$	[24597-12-4]	170.4		orthorhombic	Pnma
$Ga(Ga_2Cl_7)$	[24688-86-6]	dec 77.3	2.74	orthorhombic	$Pna2_1$
$GaCl_3$	[13450-90-3]	77.8	2.47	triclinic	$P\bar{1}$
$Ga(GaBr_4)$	[18897-61-5]	164.5	3.471		α
$Ga(Ga_2Br_7)$	[50647-37-5]	dec 81.2	3.631	orthorhombic	$P2_12_1$
$GaBr_3$	[13450-88-9]	124.1	3.74	orthorhombic	Pbca
$Ga(GaI_4)$	[17845-89-5]	211			
GaI_3	[13450-91-4]	212	4.15	monoclinic	$P2_1/c$

[a] Two forms exist, having a transition at 152°C.

11.2. Halides. *Gallium(I).* Halides of Ga(I) are known only in the vapor phase. Coordination complexes of GaCl and GaBr have been obtained with dioxane, morpholine, and acetylacetone.

Gallium(I)-Gallium(III). Compounds having the formula Ga_2X_4 where X = Cl, Br, or I, are known. The structure of these mixed valance compounds, Ga^+-$(GaX_4)^-$, has been better understood in recent years (69,70). Some properties are listed in Table 9. Other compounds such as $Ga^+(Ga_2X_7)^-$, where X=Cl or Br, have also been identified and the structures determined (71,72).

Gallium(III). Anhydrous gallium(III) fluoride [7783-51-9], GaF_3, is obtained as colorless needles, which dissolve slowly in water, by thermal decomposition of ammonium hexafluorogallate(III) [14639-94-2] in a stream of argon. The hydrate, $GaF_3 \cdot 3H_2O$ [22886-66-4], obtained by dissolving metallic gallium or the hydroxide in hydrofluoric acid, is more soluble in water. Thermal decomposition of $GaF_3 \cdot 3H_2O$ yields the hydroxyfluoride, $16[Ga(OH,F)_3]\cdot 6H_2O$, which is fcc at 200°C (73). Between 350 and 500 MPa (3450-4940 atm) at 300°C (74), the reaction of HF and Ga_2O_3 yields another hydroxyfluoride, $Ga_8[(OH)_{0.45}$-$F_{0.55}]_{24}\cdot 3H_2O$, which is of the pyrochloro cubic type.

Gallium trichloride [13450-90-3], $GaCl_3$, forms as colorless needles upon reaction of chlorine or HCl and gallium at ca 200°C in a stream of nitrogen. An airtight apparatus is used to exclude traces of moisture. $GaCl_3$ can be purified by distillation in a stream of chlorine or nitrogen. Its structure seems to be a bridged dimer molecular lattice. A hydrate, $GaCl_3 \cdot H_2O$ [23306-52-7], mp 44.4°C, is known. The gallium trichloride is extremely soluble in water, ie, >800g/L.

Gallium hydroxychloride [73157-09-2], $GaCl_2OH$, can be obtained (75) by decomposition at 130°C of the complex, $GaCl_3 \cdot C_2H_5OH$ [19379-37-4]. The hydroxychloride melts at 120°C and is a cyclic tetramer.

Gallium tribromide [13450-88-9], $GaBr_3$, is obtained by reaction of a stream of bromine vapor and nitrogen on gallium. The tribromide has seven hydrates, $GaBr_3 \cdot xH_2O$, where x=1, 2, 2.5, 3, 4, 6, or 15 (76). Gallium hydroxybromide [73157-08-1], $GaBr_2OH$, which melts at 175°C, can be obtained by the same method as used for the hydroxychloride.

Gallium triiodide [13450-91-4], GaI_3, is obtained by direct reaction of the elements or by reaction of iodine solution in carbon disulfide on gallium.

Gallium Oxyhalides. The compounds gallium oxychloride [15588-51-9], GaOCl, and galliumoxybromide [15605-97-7], GaOBr, are obtained by reaction of Ga_2O_3 on $GaCl_3$ or $GaBr_3$ in a sealed tube at ca 300°C. These materials crystallize in the orthorhombic system.

Gallium Halogenates. The anhydrous gallium(III) perchlorate [19854-31-0], $Ga(ClO_4)_3$, is obtained by reaction of chlorine peroxide, Cl_2O_6, on $GaCl_3$ at -180°C (77). The product is a white solid and is stable at room temperature.

Sulfohalides and Sulfohalogenates. Gallium(III) fluorosulfide [73157-10-5], GaSF, is obtained by heating Ga_2S_3 and GaF_3 under pressure at 310°C. The sulfohalides, $Ga_9S_8Cl_{11}$ [12268-03-0] and $Ga_9S_8Br_{11}$ [12049-26-2] are monoclinic solids, obtained by heating Ga_2S_3 and $GaCl_3$ in a sealed tube at 250°C, or $GaBr_3$ at 330°C, respectively (78). The gallium(III) chlorosulfite [30338-20-6], $Ga(SO_3Cl)_3$, and its addition compounds with LiCl and NaCl, were also obtained (79).

Compounds with Ammonia. Gallium halides give the following derivatives with ammonia: $GaF_3 \cdot NH_3$ [73157-06-9] and $GaF_3 \cdot 3NH_3$ [36171-86-5]; $GaCl_3 \cdot NH_3$ [50599-24-1]; $GaBr_3 \cdot NH_3$ [54955-92-9]; $GaI_3 \cdot NH_3$ [58384-90-0]. Some poorly defined compounds of gallium chloride, bromide, and iodide that contain up to 14 NH_3 groups also exist.

Other Halides. Hexafluorogallates(III), M_3GaF_6, are known where M is a univalent element, M = Cs [16027-80-8], K [16061-04-4], Li [16061-07-7], Na [16061-62-4], Rb [16061-06-6], Tl [26846-24-2], and NH_4 [14639-24-2], Tetrafluorogallates, $MGaF_4$, where M = Cs [15002-96-7], K [15002-94-5], Li [39210-67-8], Na [15002-93-4], Rb [15002-95-6], Tl [26667-61-8], and NH_4 [18532-60-0], also exist. There are also pentafluorogallates(III). Some typical examples are the compounds of $MGaF_5$, where M is Ca [27658-92-0], Cd [58984-51-3], Mn [35745-87-0], Pb [27658-94-2], or Sr [27658-93-1].

Two types of chlorogallates(III) are known (40,42): $MGaCl_4$, where M = Cs [21646-31-1], K [18154-89-7], or Rb [21646-29-7]; and MGa_2Cl_7, where M = Cs [12331-25-8], K [30617-31-1], or Rb [56531-09-0]. These are analogous to the mixed valence compounds, ie, $M = Ga^+$. Additionally, the following chlorogallates(III) are also known, but less precisely: $MGaCl_4$ where M = In [12432-57-4], Li [15955-98-3], Na [15007-28-0], or Tl [26490-70-0]; and several $M(GaCl_4)_2$ and $MGaCl_5$ compounds. The chlorogallate(III) $GaSbCl_6$ [73157-05-8] has been studied (32). Chlorogallates(III) are also obtained with $AsCl_3$, $AsCl_5$, PCl_3, PCl_5, $POCl_3$, $SeCl_4$, $TeCl_4$, $MoCl_5$, $NbCl_5$, and $TaCl_5$.

The following bromogallates(III) have been described (38,40): $MGaBr_4$ where M = Cs [52582-09-9], K [50328-30-8], or Rb [52582-08-8]; MGa_2Br_7 where M = Cs [52724-44-4], K [39681-16-8], or Rb [52582-11-3]; and MGa_3Br_{10} where M = Cs [62974-40-7], or Rb [62974-41-8]. The bromogallate(III) $SbGaBr_6$ [12514-56-6] also was studied (69). Three types of iodogallates (III) have been described (80): $MGaI_4$ where M = Cs [57146-51-7] or Rb [57146-50-6]; MGa_2I_7 where M = Cs [57143-24-5] or Rb [57143-25-6]; and $SbGaI_6$ [12519-02-7] (69).

Gallium trihalides, particularly $GaCl_3$ and $GaBr_3$, form a large number of complexes with organic Lewis bases. Complexes are also formed with other compounds, especially those containing, O, S, N, P, or As, eg, $LGaCl_3$, where

Table 10. **Gallium Oxides and Hydroxides**

Compound	Means of preparation	Crystal structure
Ga_2O	reduction of Ga_2O_3 with Ga at 500–600°C, under vacuum	
α-Ga_2O_3	heating GaOOH at 300–500°C	trigonal, $R\bar{3}C$ (corundum α-AlO_3)
β-Ga_2O_3	calcination at $\geq$600°C of $Ga(OH)_3$ or other salts	monoclinic, C2/m (β-Al_2O_3)
γ-Ga_2O_3	rapid dehydration on gels at ca 400°C	cubic, Fd3m (spinel)
δ-Ga_2O_3	by decomposition of $Ga(NO_3)_3$ at ca 250°C	cubic, Ia3(MnO_3)
ϵ-Ga_2O_3	brief heating of δ-Ga_2O_3 at ca 550°C	orthorhombic (κ-Al_2O_3)
GaOOH	oxidation of Ga with H_2O at ca 200°C, under pressure	orthorhombic Pbnm (diaspore)
Ga(OH)3	neutralization of aqueous Ga(III) salts or alkaline gallates (III)	unstable gel

$L = (C_2H_5)_2O$ or pyridine. Generally, because of its acceptor strength, the reactivity of trivalent Ga is ranked below aluminum and above indium and boron.

11.3. Gallium Oxides. The preparation conditions of gallium oxides and hydroxides are listed in Table 10.

Gallium(I). Gallium(I) oxide [12024-20-3], Ga_2O, is a dark brown powder, stable in cold, dry air, and has a density of 4.77 g/cm^3. Above 700°C, it decomposes into gallium and Ga_2O_3.

Gallium(III). Ga_2O_3 is the single gallium oxide that is stable under normal conditions. Like alumina, it exists in several crystalline forms. The most stable form is the beta oxide, mp ca 1725°C, density 5.88 g/cm^3. The density of α-Ga_2O_3 is 5.18 g/cm^3.

Gallium(III) oxide [12024-21-4] can be reduced at ca 600°C by hydrogen, carbon monoxide, or metallic gallium. It is more reactive than alumina and is strongly amphoteric, forming gallium salts with acids and gallates(III) with bases. There is only one well-defined hydroxide, gallium(III) oxide monohydrate [20665-52-5], GaOOH or $Ga_2O_3 \cdot H_2O$. The gallium(III) hydroxide [12023-99-3], $Ga(OH)_3$, probably has an amorphous structure.

11.4. Gallates(III). Use of the oxidation number (III) was recommended by the IUPAC to distinguish gallates(III) from the salts of gallic acid, 3,4,5-trihydroxybenzoic acid, which often are wrongly named gallates. The alkali metal gallates(III) are the only gallates(III) that are soluble in water; the former gives stable solutions at all concentrations, unlike aluminate solutions. They are obtained easily by direct reaction of metallic gallium with solutions of the hydroxides of Na, K, Rb, or Cs. The ratio M:Ga can be as low as unity; the solutions can be obtained in very high concentration by evaporation, eg, 800 g Ga/L solution for the sodium gallate(III). Lithium gallate(III) is less soluble than $NaGaO_2$.

The solid gallates(III) of numerous elements have been studied and include gallates(III) of alkaline and other metals. The former group includes Li_5GaO_4, $LiGaO_2$, and $LiGa_5O_8$; $MGaO_2$ where M = Cs, K, Na, or Rb; and $Na_2O_5 \cdot 4Ga_2O_3$ and $Na_2O \cdot 7Ga_2O_3$ (ionic conductors, of the type of β alumina). The latter group includes $MGaO_2$ (M=Cu or Ag); MGa_2O_4 (M=Ba, Sr, Co, Cu, Fe, or Zn);

Table 11. **Gallium Chalcogenides**

Compound	CAS Registry number	Mp, °C	Crystal structure	Density g/cm^3
GaS	[12024-10-1]	962	hexagonal (lamellar)	3.86
Ga_2S_3	[12024-22-5]	1090	monoclinic, Bb (superstructure of wurtzite type)	3.77
GaSe	[12024-11-2]	960–965	hexagonal (lamellar)	5.01
Ga_2Se_3	[12024-24-7]	1005–1010	monoclinic, B2/m (superstructure of deformed blend type) cubic by quenching of liquid compound (disordered sphalerite type)	4.95
GaTe	[12024-14-5]	825	monoclinic or hexagonal (lamellar structure)	5.44
Ga_2Te_3	[12024-27-0]	792	cubic (sphalerite type)	5.57
Ga_2Te_5	[73623-48-0]	stable	tetragonal only at 400–495°C	5.85

$CaO \cdot nGa_2O_3$ (n=0.33, 1 or 2); $AlGaO_3$; and $LnGaO_3$ and $Ln_3Ga_5O_{12}$ with the lanthanides. Among these compounds, a number are studied for their useful magnetic or electric properties, especially spinels, perovskites, and above all, garnets, eg, $Ln_3Ga_5O_{12}$ (Ln=Dy, Sm, or Gd) (see FERROELECTRICS).

11.5. Gallium Chalcogenides.

Gallium forms two types of compounds by reaction with sulfur, selenium, and tellurium, and these are listed in Table 11. One type is represented by GaS, GaSe, and GaTe, in which the gallium is trivalent and the form is a lamellar crystal containing atomic groups such as S–Ga–Ga–S. In such a group, each gallium atom is surrounded by a tetrahedron containing 3 S and 1 Ga. This lamellar structure gives two-dimensional properties to these semiconductor compounds (see SEMICONDUCTORS, SILICON-BASED SEMICONDUCTORS). The other compound type includes Ga_2S_3 (81), Ga_2Se_3 (82), and Ga_2Te_3, which have vacancies in their structure that also give particular electronic properties.

Mixed Chalcogenides. The mixed chalcogenides include $MGaS_2$ (or Se_2 or Te_2), where M = Ag, Cu, In, or Tl; among these compounds, some are semiconductors, eg, $AgGaS_2$ [12002-67-4] or $CuGaS_2$ [12018-83-6]. Other mixed chalcogenides are MGa_2S_4 (or Se_4 or Te_4) where M= Cd, Hg, or Zn; $MGaS_3$, where M = In [12398-40-2] or Y [12018-83-6]; and $M_{18}Ga_{10}S_{42}$ (or Se_{42}), where M = lanthanides.

Sulfates and Selenates. The anhydrous gallium(III) sulfate [13494-91-2], $Ga_2(SO_4)_3$, is obtained by dissolving GaOOH in 50% H_2SO_4, evaporating, filtering, and drying to 360°C. It crystallizes from aqueous solutions as $Ga_2(SO_4)_3 \cdot 18H_2O$. In the presence of alkali metal or ammonium sulfates, it gives alums, $MGa(SO_4)_2 \cdot 12H_2O$, where M is Cs, K, Rb, or NH_4. Gallium selenate is obtained under the same conditions as the sulfate. Like the sulfate, it gives double selenates that are isomorphous with alums.

11.6. Gallium Nitrogen Compounds. Direct combination of gallium and nitrogen (83) involves a gas discharge at 750°C for the dissociation of N_2 into atomic N which combines with Ga vapor; a thin film of GaN is deposited. Gallium nitride [25617-97-4] can also be obtained by the reaction of ammonia on gallium at ca 1000°C, or on gallium compounds (oxide, chloride, sulfide, etc). GaN is also prepared by thermal decomposition of triammonium hexafluorogallate(III) in a stream of ammonia at ca 600°C. Gallium nitride, hexagonal, wurtzite type, density, 6.10 g/cm^3, is very stable in air at ca 900°C; it can be sublimed in a stream of ammonia at 1150°C. It has a colorless crystal form when pure. It is a semiconductor and as such promises practical applications, especially as an electroluminescent compound. Double nitrides with metals, particularly the alkali metals, are known, eg, Li_3GaN_2. The hydrated nitrate, $Ga(NO_3)_3 \cdot 9H_2O$, is formed by dissolving gallium in nitric acid.

Gallium(III) azide [73157-11-6], $Ga(N_3)_3$, is prepared by decomposition, at 250°C, of the addition compound $GaF_3{\cdot}NH_3$ [73157-06-9].

Contrary to previous indications apparently gallium boride does not exist.

11.7. Gallium Compounds with Phosphorus, Arsenic, and Antimony. The 1:1 compounds, gallium phosphide [12063-98-8], GaP, gallium arsenide [1303-00-0], GaAs, and gallium antimonide [12064-03-8], GaSb, can be obtained by direct combination of the elements at high temperature. GaP and GaAs formation requires combination under pressure. The three compounds also can be prepared, mainly as thin films, by numerous exchange reactions in the vapor phase.

Gallium phosphide, density=4.13g /cm^3, melts at 1465°C under pressure; gallium arsenide, density=5.360g /cm^3, melts at 1238°C under pressure; and gallium antimonide, density=6.096g /cm^3 melts at 712°C. All three crystallize in the cubic system (sphalerite type) and possess semiconductor properties which make these materials, especially the arsenide, the most important in terms of practical applications of gallium. Many mixed compounds also are used, eg, $GaAs_{1\text{-}x}\,P_x$ or $Ga_{1\text{-}x}Al\,_xAs$ (see LIGHT-EMITTING DIODES; OPTICAL DISPLAYS; SEMICONDUCTORS, SILICON-BASED SEMICONDUCTORS).

Gallium phosphates are obtained by the reaction of gallium hydroxide on the phosphorus oxoacids. Anhydrous gallium phosphate is prepared by heating the dihydrate or by the reaction of gallium on phosphoric acid in a sealed tube at 200°C. Anhydrous gallium phosphate [14014-97-2], $GaPO_4$, hexagonal (beta quartz type); hydrated phosphate, $GaPO_4{\cdot}2H_2O$ [23653-37-4], orthorhombic; and pyrophosphates, $GaHP_2O_7$ [34641-69-5] and $Ga_4(P_2O_7)_3 \cdot xH_2O$ [19584-43-1] (xabout=23), are known.

Anhydrous gallium arsenate [13811-89-7], $GaAsO_4$, hexagonal (beta quartz type) is slightly soluble in water and can be obtained by the reaction of $GaCl_3$ on As_2O_3 at 800°C. It forms a hydrate, $GaAsO_4{\cdot}2H_2O$ [23653-38-5] which is orthorhombic, and it can form acidic salts, eg, $Ga(H_2AsO_4)_3 \cdot xH_2O$ with $x = 1$ [38296-94-5] or $x = 5$ [38296-97-8].

Gallium antimonate [28888-33-7], $GaSbO_4$, is tetragonal (rutile type) and has a density of 6.540 g/cm^3.

11.8. Carbon Compounds of Gallium. There is no binary gallium carbide; however, some ternary carbides have been studied, principally with regard to their structure and magnetic properties: Mn_3GaC [12069-65-7],

Nd_3GaC [12127-26-3], and Mo_2GaC [12286-91-8] (see CARBIDES, SURVEY; MAGNETIC MATERIALS, BULK).

More than 1000 organic gallium compounds have been described in addition to the coordination compounds of the gallium hydride or halides already mentioned. These compounds include salts of organic acids, eg, acetate, oxalate, citrate, and numerous complexes, eg, oxalates, $Ga(C_2O_4)^+$, $Ga(C_2O_4)^{2-}$, $Ga(C_2O_4)_3^{3-}$; alkoxides or their derivatives by substitution, eg, $Ga(OCH_3)_3$ [2746-72-7], $Ga(OC_2H_5)_3$ [2572-25-0], $Ga(OC_6H_5)_3$ [2572-17-0], and $GaCl(OCH_3)_2$ [21907-51-7], and $GaCl_2(OCH_3)$ [22381-97-1]. Another group is the organogallium compounds, R_3Ga, which contain Ga-C bonds, where R is methyl [1445-79-0] (mp-15.8°C), ethyl [1115-99-7] (mp 82.3°C), *n*-propyl [29868-77-7], isopropyl [54514-59-9], propenyl (cis or trans), butyl [15677-44-8], pentyl [15677-45-9], hexyl, decyl, phenyl [55321-79-4], and α-naphthyl. In addition, a number of their substitution or coordination compounds have been described.

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