trap held at −131°. The −131° condensate was unreacted $(CH_3)_2AsH$ (134.6 mg, 1.270 mmol; mol wt: calcd, 106.0; found, 105.3; confirmed by infrared spectrum[30]). From the stoichiometry of the reaction, the dark red residue remaining in the reaction vessel was $[(CH_3)_2AsCo(CO)_3]_x$ (33.6 mg, 0.136 mmol; 100% yield based on the quantity of $HCo(CO)_4$ employed).

(B) Arsine.—AsH_3 (126.9 mg, 1.628 mmol), C_2H_4 (78.8 mg 2.81 mmol), and $HCo(CO)_4$ (82.6 mg, 0.480 mmol) were condensed into a 4.5-ml reaction vessel. A yellow solution was observed after holding the contents at −45° for 15 min, and a black solution was observed after 25 min at −35°. After 15 min at −23°, 30 min at −15°, and 15 min at room temperature it was held at −196° for 5 min before removing a large quantity of noncondensable material (possibly CO and/or H_2).

A mixture of unreacted C_2H_4 and AsH_3 (identified by infrared spectra;[23,38] from mol wt, 78.8 mg (2.81 mmol) of C_2H_4 and 87.4 mg (1.12 mmol) of AsH_3) was recovered as the more volatile fraction passing through a trap held at −131°. The −131° condensate was impure $HCo(CO)_4$ (10.7 mg, 0.0622 mmol; identified by infrared spectrum[35]). A solid residue remaining in the reaction vessel weighed 97.0 mg.

Notes

Contribution from Scientific Laboratory,
Ford Motor Company, Dearborn, Michigan 48121

The Preparation of Gallium(I) β-Alumina

By R. H. Radzilowski

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Monovalent gallium compounds have been reported in the literature since 1930,[1,2] but only in recent years have structural studies[3,4] confirmed the existence of the Ga^+ ion in crystalline materials. This paper reports the preparation of a crystalline Ga(I) compound by an ion-exchange method in which silver in silver-substituted β-alumina is replaced mole for mole by gallium.

Beevers and Ross[5] have determined the crystal structure of sodium β-alumina and found that for the ideal, fixed occupation of all atomic sites in the crystal lattice the formula $Na_2O \cdot 11Al_2O_3$ is required. Sodium analyses of clear, single crystals have shown that the chemical formula varies between $Na_2O \cdot 9Al_2O_3$ and $Na_2O \cdot 10.5Al_2O_3$. Nevertheless, Yao and Kummer[6] have reported that sodium β-alumina exchanges all of its Na^+ ions for other cations (*e.g.*, Ag^+, K^+, Rb^+, Li^+, Tl^+, NH_4^+) in molten salts without altering the basic β-alumina structure, and the exchange is reversible giving back the original sodium β-alumina. In all cases, the resulting compounds are isomorphous with $Na_2O \cdot 11Al_2O_3$. From the known properties of sodium β-alumina and experiments described below, it is most probable that the gallium species in gallium(I) β-alumina is the Ga^+ ion.

Experimental Section

Single crystals of gallium(I) β-alumina were prepared by exchanging Ag^+ ions in silver(I) β-alumina[7] with Ga^+ ions in a melt containing metallic gallium and gallium iodide. Pure gallium metal and solid iodine were mixed in the mole ratio of 5 : 1 with single crystals of silver(I) β-alumina in a quartz tube which was evacuated, sealed, and heated at 285° for 16 hr. The melt to crystal volume ratio was 10 : 1. The melt was dissolved in dilute hydrochloric acid leaving a pool of gallium–silver metal and the gallium(I) β-alumina crystals which were transparent and reddish brown. The average thickness and diameter of the single crystals were 0.15 mm and 1 mm, respectively. After one exchange 99.6% of the Ag^+ ions were replaced by Ga^+ ions. A second exchange in a freshly prepared melt removed the remaining detectable silver leaving at most 0.02 wt % Ag. The gallium content of completely exchanged samples ranged from 11.96 to 12.91 ± 0.03 wt % Ga with $\leq$0.02 wt % Ag. The chemical analyses were obtained by atomic absorption spectroscopy using a Techtron AA (Cary Instruments, Inc., Monrovia, Calif.). X-Ray powder diffraction data were obtained with a Debye–Scherrer 114.59-mm camera. The samples were ground to 60-μ size and packed in 0.3-mm glass capillaries. Samples were exposed to Ni-filtered Cu Kα radiation for 5 hr on a Norelco X-ray generator. Intensities of reflections were measured on a double-beam recording microdensitometer (Joyce, Loebl and Co., Ltd., Gateshead, England). The thermogravimetric analyses were made on the R. G. automatic electrobalance (Cahn Instrument Co., Paramount, Calif.).

Discussion

Gallium(I) β-alumina is isomorphous with the hexagonal layer structure of $Na_2O \cdot 11Al_2O_3$[5] which has the space group P6/mmc, with one molecule per unit cell. The lattice constants of gallium(I) β-alumina, $Ga_2O \cdot 11Al_2O_3$, containing 12.9 wt % Ga are $a_0 = 5.600$ and $c_0 = 22.718$ Å determined from a Debye–Scherrer powder pattern and refined by a least-squares method. The diffraction pattern for gallium(I) β-alumina is given in Table I.

The variation of gallium in gallium(I) β-alumina

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[5] C. A. Beevers and M. A. S. Ross, *Z. Krist*, **97**, 59 (1937); the X-ray powder pattern data are listed and indexed in ASTM X-Ray Powder Data File 1-1300.

[6] Y. F. Yu Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.*, **29**, 2453 (1967).

[7] The β-alumina used was obtained from fused cast bricks (Monofrax H) made by the Harbison Carborundum Co., Falconer, N. Y. This material when placed in $AgNO_3$ melt for 2 hr produced silver β-alumina by ion exchange. A chemical analysis showed complete exchange of Na^+ ions for Ag^+ ions.

TABLE I
POWDER PATTERN FOR $Ga_2O \cdot 11Al_2O_3$
(FORWARD-REFLECTED REGION)

I/I_0	d_{obsd}, Å	d_{calcd}, Å	*hkl*
97	11.4	11.36	002
29	5.68	5.68	004
5	4.85	4.85	100
7	4.75	4.74	101
64	4.46	4.46	102
3	3.79	3.79	006
12	3.70	3.69	104
5	3.33	3.32	105
17	2.84	2.840	008
55	2.81	2.800	110
100	2.71	2.718 2.697	112 107
82	2.52	2.511	114
23	2.42	2.425 2.411	200 201
19	2.37	2.371	202
9	2.31	2.309	203
13	2.27	2.272	0,0,10
15	2.25	2.251	116
13	2.23	2.229	204
48	2.14	2.139	205
11	2.05	2.057	1,0,10
41	2.04	2.042	206
19	1.94	1.942	207
13	1.84	1.844	208
2	1.81	1.809	212
5	1.76	1.764	1,1,10 1,0,12
5	1.74	1.749 1.744	209 214
6	1.66	1.658	2,0,10
9	1.62	1.623 1.616	0,0,14 300
30	1.60	1.600 1.596	302 217
27	1.57	1.572 1.568	2,0,11 1,1,12
14	1.56	1.555	304
6	1.54	1.539	1,0,14
8	1.487	1.487	306
7	1.426	1.426	2,1,10
27	1.419	1.420 1.418	0,0,16 2,0,13
59	1.400	1.400	220
7	1.389	1.389	222
5	1.359	1.359	224
23	1.349	1.349	2,0,14
4	1.266	1.266	1,1,16
2	1.257	1.256	228
7	1.242	1.242	317

from sample to sample is in agreement with the 4.3–5.0 wt % Na variation found in the starting material, sodium β-alumina. From the chemical analyses, the $Ga_2O : Al_2O_3$ mole ratio is closer to 1 : 10 than to 1 : 11. The calculated density and gallium content of the stoichiometric $Ga_2O \cdot 11Al_2O_3$ are 3.44 g/cm^3 and 10.92 wt % Ga, respectively. The measured density of gallium(I) β-alumina containing 12.65 wt % Ga is 3.51 g/cm^3. This density value can be calculated from the measured density of 3.24 g/cm^3 for sodium β-alumina which contains 4.6 wt % Na, when assuming that all of the Na^+ ions are replaced by Ga^+ ions and correcting for the change in lattice parameters.

Thermogravimetric analysis of gallium(I) β-alumina showed a slow weight increase ($\sim$1%) in dry air beginning at $\sim$750° over a 72-hr period. A pickup of oxygen and subsequent oxidation of some Ga^+ ions would account for the increase in weight. A chemical analysis showed no loss of gallium from the sample. An X-ray powder diagram of the product contained all of the diffraction lines due to the β-alumina structure, but there was an increase in the intensity and broadening of the 1.39- and 2.37-Å *d* spacings. These two *d* spacings were later found to be the most intense lines in the X-ray pattern of the new product resulting from heating gallium(I) β-alumina *in vacuo* at 900°. This seemed to indicate that a new phase(s) had started to form. Gallium(I) β-alumina which was exposed to moist air for 5 months did not lose any detectable weight when heated to 600° in dry air.

The reddish brown color of 60-μ size gallium(I) β-alumina was bleached in air at 540°. Since the lattice constants remained unchanged and no appreciable weight change was found, the color is probably due to a small excess of gallium atoms in the crystal lattice which produced color centers rather than being characteristic of the Ga^+ ion.

Heating the gallium(I) β-alumina in platinum foil at 900° *in vacuo* for 16 hr caused two-thirds of the gallium to react with the platinum as evidenced by the change in appearance and the increase and decrease in weight of the platinum and β-alumina, respectively, and an X-ray powder pattern of the Pt–Ga material. An X-ray powder pattern of the black gallium alumina product did not have lines or intensities indicative of the β-alumina structure. Two *d* spacings of high intensity appeared at 1.39 and 2.37 Å with several broad, weak *d* spacings at 3.79, 2.25, 2.04, 1.95, 1.52, 1.24, 1.17, and 1.025 Å. The Ga^+ ions in gallium(I) β-alumina probably disproportionated into Ga^{3+} ions and Ga^0 atoms. Since the vapor pressure of gallium is $\sim 10^{-3}$ mm at 900°, the Ga^0 could diffuse out of the β-alumina leaving behind one-third of the gallium as Ga^{3+} ions. It was not known how the Ga^{3+} ions were incorporated in this product. However, when this material was heated at 1300° for 3 hr in air and quenched, the black color disappeared and the resulting product was identified from X-ray diffraction data and chemical analysis as a Ga_2O_3–Al_2O_3 solid solution[8] containing 4.1 mol % Ga_2O_3 and being isomorphous with α-Al_2O_3.

The gallium in gallium(I) β-alumina was replaced by Na^+ ions in an NaCl melt at 810° without altering the β-alumina structure.

Conclusions

Gallium(I) β-alumina is nonhygroscopic and stable in air at least to 600°. Sodium ions in sodium β-alumina

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(8) V. G. Hill, R. Roy, and E. F. Osborn, *J. Am. Ceram. Soc.*, **35** (6), 138 (1952).

are completely exchanged for silver ions which in turn are replaced by gallium ions on a mole for mole basis without altering the β-alumina structure. The mean valence state of the gallium in gallium(I) β-alumina is +1. The possibility of gallium existing in a mixed valence state (Ga^{3+},$2Ga^0$) in the aluminum oxide lattice seems improbable because two-thirds of the gallium would be Ga^0 atoms which are not expected to be stable while dispersed in an oxide and would therefore separate into a metallic Ga phase leaving the crystals opaque. The gallium(I) β-alumina can be prepared as transparent, colorless single crystals. It is concluded that the gallium exists as Ga^+ ions in the β-alumina lattice.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

Reactions of Triphenylgermyl Bromide with Ammonia and of Tri-*n*-propyltin Chloride with Ammonia and Sodium Amide

BY RONALD E. HIGHSMITH
AND HARRY H. SISLER

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We have noted that the report of the synthesis of tris(triphenylgermyl)amine by Kraus and Wooster[1] in 1930 continues to be listed in recent reviews.[2–4] No other report of the synthesis of this compound appears in the literature. We have found that the "calculated" percentage of nitrogen for $[(C_6H_5)_3Ge]_3N$ given by Kraus and Wooster in their paper is incorrect, and have repeated their procedure with results which indicate that the product obtained is not $[(C_6H_5)_3Ge]_3N$, but rather is $[(C_6H_5)_3Ge]_2NH$. Since the reaction of triphenylgermanium bromide and ammonia has been shown to yield bis(triphenylgermyl)amine instead of tris(triphenylgermyl)amine, it can now be observed that this reaction is analogous to the reaction of trialkylgermanium halides with ammonia or sodium amide[5,6] in that the secondary rather than the tertiary amine is formed.

Only three tris(trialkylstannyl)amines have been reported: $[(CH_3)_3Sn]_3N$,[7] $[(C_2H_5)_3Sn]_3N$,[8] and $[(n\text{-}C_3H_7)_3Sn]_3N$.[8] There is no reason to doubt the identification of the first compound, since Lehn[9] confirmed it by molecular weight determination in 1964. However, since no molecular weight determinations have been made on the remaining two compounds, their identification must be subject to some doubt, since the expected elemental analyses of corresponding tertiary and secondary compounds, such as $[(n\text{-}C_3H_7)_3Sn]_3N$ and $[(n\text{-}C_3H_7)_3Sn]_2NH$, are very similar. We have repeated the procedures of Sisido and Kozima[8] and have isolated two compounds, $[(n\text{-}C_3H_7)_3Sn]_2NH$ and $[(n\text{-}C_3H_7)_3Sn]_3N$, instead of one as previously reported. This is the first report of a distannyl-substituted amine having an NH bond. No attempt was made to maximize the yield of either product. We suggest that the compound isolated by Sisido and Kozima may have been $[(n\text{-}C_3H_7)_3Sn]_2NH$, rather than $[(n\text{-}C_3H_7)_3Sn]_3N$ as claimed by them; however, this suggestion is based solely on comparison of boiling points, since this was the only property given in their report. It should be recognized that comparison of boiling points obtained under reduced pressure is often not reliable. However, regardless of boiling point considerations, the fact remains that two distinct compounds were obtained when only one was previously reported.

Experimental Section

Elemental analysis of the germanium compound was carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and of the tin compounds by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points (uncorrected) were obtained using a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained with a Beckman IR-10 spectrophotometer using potassium bromide disks. Mass spectral data were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer at an ionizing voltage of 70 eV, calibrated at $m/e = 200$. Proton magnetic resonance spectra were obtained with a Varian A-60A instrument.

Triphenylgermanium bromide was prepared from tetraphenylgermane according to the procedure of Kraus and Foster[10] (mp 136–139°, lit.[10] mp 138.7°). Tri-*n*-propyltin chloride was used as purchased from Alfa Inorganics, Inc. Reagent grade solvents were dried by storing over calcium hydride in the inert atmosphere box. All operations such as transfers, filtrations, and preparation of samples for determination of their infrared and nuclear magnetic resonance spectra were carried out in the inert atmosphere box, Dri-Lab Model HE-43 with Dri Train HE-93B, from Vacuum Atmospheres, Inc.

Reaction of Triphenylgermanium Bromide with Ammonia.—A procedure, analogous to the reported procedure of Kraus and Wooster,[1] was used. Ammonia was introduced into a solution of 3.07 g of triphenylgermanium bromide in 50 ml of carbon tetrachloride until no further reaction was noted at room temperature and the mixture was left to stand for 24 hr. It was filtered and the solvent was removed from the filtrate by distillation under reduced pressure. It was warmed to 205° for 4 hr and then held under reduced pressure to remove the ammonia. The liquid solidified upon cooling. It was recrystallized from hot petroleum

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