Chem. Mater. **1990**, 2, 221–222

While investigating tungstic acids, Freedman[8] had isolated two sodium-containing phases labeled as phase C and phase X. Although they[13] did not analyze their diffractograms, our indexing/least-squares analysis of their data indicates that these are hexagonal (with a = 7.317 Å and c = 7.773 Å) and cubic (a = 10.26 Å) phases similar to what we have obtained in this study. Their patterns however contained additional lines presumably due to impurity phases; we believe that the use of the hydrothermal technique reported here has assisted in the formation of impurity free phases. They report one composition for the X phase corresponding to $(Na_2O)_{0.29}WO_3{\cdot}1.1H_2O$, not dissimilar to the composition found here; their titration data suggest that a significant proportion of the sodium can be exchanged for hydrogen.

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[13] Freedman, M. L.; Leber, S. *J. Less Common Met.* **1964**, 7, 427.

Preparation of Indium Antimonide Using a Single-Source Precursor

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The narrow bandgap and high electron mobility of InSb render this material very attractive for high-speed circuits, infrared detectors, and novel quantum well devices. Several techniques have been employed for the preparation of InSb;[1] however, the production of this material by organometallic chemical vapor deposition (OMCVD) has been relatively little explored.[2] We report the first example of the use of a single-source precursor for the deposition of InSb. Preliminary experiments indicate that this method is also valid for GaSb preparation.

In designing an appropriate precursor, we sought systems with strong In–Sb bonds and with hydrocarbon groups capable of undergoing clean, facile decomposition. By analogy with our GaAs precursor,[3] we decided on a target molecule of the type $[Me_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_n$. Initial experiments indicated that the chemistry of Sb to be significantly different from that of As and P. For example, the reaction of $t\text{-Bu}_2SbSiMe_3$ with $InCl_3$ afforded the 1:2 stoichiometry product $[(t\text{-Bu}_2Sb)(Cl)In(\mu\text{-Sb-}t\text{-Bu}_2)]_2$ regardless of the reactant mole ratio employed.[4] Moreover, attempts to prepare $[Me_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_n$ by methylation of $[Cl_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_3$ met with failure. We have now succeeded in the preparation of $[Me_2In(\mu\text{-Sb-}t\text{-Bu}_2)]_3$ (**1**) via the following sequence of steps:

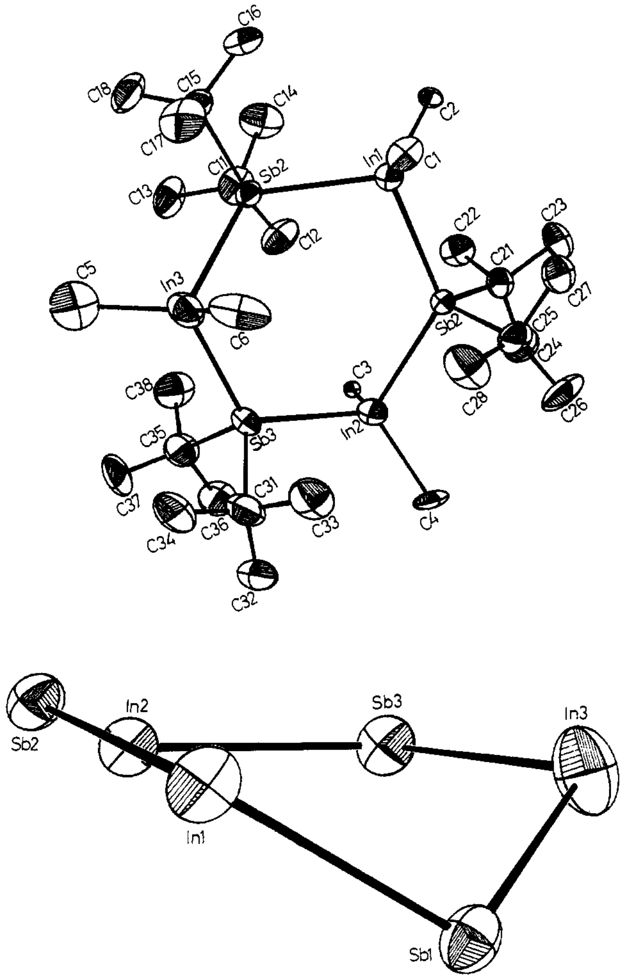

Figure 1. Top: view of **1** showing the atom numbering scheme. Bottom: In_3Sb_3 skeleton of **1**. Important bond distances (Å) and angles (deg): In(1)–Sb(1), 2.822 (1); In1)–Sb(2), 2.889 (1); In(2)–Sb(2), 2.864 (1); In(2)–Sb(3), 2.838 (2); In(3)–Sb(3), 2.858 (2); In(3)–Sb(1), 2.860 (2); Sb(1)–In(1)–Sb(2), 103.65 (5); Sb(2)–In(2)–Sb(3), 109.43 (5); Sb(1)–In(3)–Sb(3), 107.73 (5); In(1)–Sb(1)–In(3), 115.84 (5); In(1)–Sb(2)–In(2), 127.79 (4); In(2)–Sb(3)–In(3), 121.28 (6).

$$t\text{-Bu}_2SbSiMe_3 \xrightarrow{\text{EtOH}} t\text{-Bu}_2SbH \xrightarrow{\text{MeLi}} t\text{-Bu}_2SbLi \xrightarrow{Me_2InCl} \mathbf{1}$$

Di-*tert*-butylstibine and $t\text{-Bu}_2SbLi$ are new compounds; however, they are unstable at ambient temperature and can be generated only in situ. In a typical experiment, ethanol (0.38 g, 8.35 mmol) was added to a solution of 2.58 g (8.35 mmol) of $t\text{-Bu}_2SbSiMe_3$ in 50 mL of THF at −78 °C. After brief warming to room temperature (15 min) the stirred solution of $t\text{-Bu}_2SbH$ was recooled to −78 °C and treated with MeLi (5.5 mL of 1.55 M solution in hexane). The resulting solution of $t\text{-Bu}_2SbLi$ was stirred at −78 °C for 20 min, following which it was warmed to room temperature and stirred for 1 h. The $t\text{-Bu}_2SbLi$ solution was then recooled to −78 °C and added via cannula to a suspension of 1.5 g (8.35 mmol) of Me_2InCl in 25 mL of THF. After the resulting bright yellow mixture was stirred at room temperature for 90 min, all solvents and volatiles were removed by evacuation. The residue was extracted with hexane and filtered Celite to give an orange solution. Concentration and cooling of this solution (−20 °C) resulted in the formation of pale orange crystalline **1** (mp 139–141

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[1] Webb, J. B.; Halpin, C.; Noad, J. P. *J. Appl. Phys.* **1986**, 60, 2949, and references therein.

[2] Chiang, P. K.; Bedair, S. M. *J. Electrochem. Soc.* **1984**, 131, 2422.

[3] Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B. Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, 110, 6248.

[4] Barron, A. R.; Cowley, A. H.; Jones, R. A.; Nunn, C. M.; Westmoreland, D. L. *Polyhedron* **1988**, 7, 77.

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°C) in 46% yield.[5] The analogous gallium compound $[Me_2Ga(\mu\text{-}Sb\text{-}t\text{-}Bu_2)]_3$ (**2**) has been prepared in 74% yield by a virtually identical procedure.[5]

X-ray analysis[6] revealed that **1** and **2** are both trimeric in the solid state. The six-membered rings of both compounds adopt a distorted twist-boat conformation that is devoid of symmetry. The structure of **1** is illustrated in Figure 1. Atoms In(1), Sb(2), Sb(3), and In(3) of **1** are approximately planar, and In(2) and Sb(1) lie 0.494 and 1.243 Å out of the idealized plane respectively. As expected, there is a significant variation in the endocyclic bond angles, particularly at antimony. The average endocyclic bond angles at In and Sb are 106.94 (5)° and 121.64 (6)°, respectively, in **1**. The In–Sb bond lengths in **1** vary from 2.822 (1) to 2.889 (1) Å. The average In–Sb bond length of 2.855 (2) Å compares with that of 2.844 (1) Å in $[(t\text{-}Bu_2Sb)(Cl)In(\mu\text{-}Sb\text{-}t\text{-}Bu_2)]_2$, the only other structurally authenticated organometallic indium stibinide.[4] Both values are close to the sum of covalent radii for In and Sb (2.84 Å) and somewhat larger than the bond distance in InSb (2.805 Å).

Films of InSb have been grown on Si(100) wafers from precursor **1** in a horizontal hot-wall reactor.[7] The temperatures of the saturator and deposition zones were 125 and 450 °C respectively, and H_2 (10 Torr) was employed as the carrier gas. Growth rates were ~1.0 μm/h. The films were characterized by X-ray photoelectron spectroscopy after etching with ionized argon. The corrected In(4d) and Sb(4d) signals at 18.5 and 33.5 eV, respectively, compare well with the literature values of 19.0 and 34–35 eV.[8] Moreover, the XPS experiments established an In:Sb stoichiometry of 1:1 and indicated that the carbon impurity level was barely above the limit of detectability by this technique (~1000 ppm). Examination of the films by X-ray diffraction indicated that they are polycrystalline. Preliminary experiments indicate that **2** is a useful precursor for the formation of GaSb.

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Registry No. **1**, 126847-96-9; **2**, 126847-97-0; $t\text{-}Bu_2SbSiMe_3$, 82363-94-8; Me_2InCl, 14629-99-3; InSb, 1312-41-0.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters (7 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(5) ^1H NMR (300 MHz, C_6D_6 TMS ext): **1**, δ 0.28 (s, 18 H, Me), 1.52 (s, 54 H, *t*-Bu); **2**, 0.41 (s, 18 H, Me), 1.52 (s, 54 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, TMS ext): **1**, δ 34.77 (s, $C(CH_3)_3$), 35.12 (s, $C(CH_3)_3$); **2**, 0.36 (s, $Ga(CH_3)_2$), 32.56 (s, $C(CH_3)_3$), 34.68 (s, $C(CH_3)_3$). The $In(CH_3)_2$ resonance for **1** was not observed. Satisfactory C and H analyses were obtained for **1** and **2**.

(6) Crystal data for **1**: $C_{30}H_{72}In_3Sb_3$, monoclinic, $P2_1/c$ (No. 14), a = 9.633 (3), b = 22.284 (6), c = 20.690(6) Å, β = 91.75°, V = 4439.3 Å^3, Z = 4, D(calcd) = 1.710 g cm^{-3}, μ(Mo Kα) = 33.4 cm^{-1}. A total of 7791 unique reflections were collected over the range $3.0 \le 2\theta \le 50.0°$ by using the $\theta/2\theta$ scan mode. Of these, 4929 were considered to be observed [$I > 3\sigma(I)$]. Crystal data for **2**: $C_{30}H_{72}Ga_3Sb_3$, monoclinic, $P2_1/c$ (No. 14), a = 9.392 (2), b = 22.080 (8), c = 20.453 (6) Å, β = 90.96 (2), V = 4240.9 Å^3, Z = 4, D(calcd) = 1.578 g cm^{-3}, μ(Mo Kα) = 37.9 cm^{-1}. A total of 7672 unique reflections were collected over the range $3.0 < 2\theta < 50.0°$ by using the $\theta/2\theta$ scan mode. Of these, 4904 were considered to be observed [$I > 3\sigma(I)$]. Both data sets were collected on an Enraf-Nonius CAD-4 diffractometer at 296 K, and corrections were made for Lorentz, polarization, and decay. The structure of **2** was solved by direct methods and that of **1** from the positional parameters for **2**. Both structures were refined by full-matrix least-squares methods. The final residuals were R = 0.053 and 0.044, and R_w = 0.060 and 0.052 for **1** and **2**, respectively.

(7) The reactor design is similar to that described by: Gladfelter, W. L.; Boyd, D. C.; Jensen, K. F. *Chem. Mater.* **1989**, *1*, 339.

(8) XPS data were obtained on a VG Scientific Escalab Mark I instrument with a Mg Kα X-ray anode. The observed binding energies were corrected for electrostatic charging by referencing to the adventitious C(1s) peak. Literature values were taken from: *The Handbook of X-ray Photoelectron Spectroscopy*; Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., Muilenberg, G. E., Eds.; Perkin-Elmer: Physical Electronics Division, 1976.

Conductive Polymer/Oxide Bronze Nanocomposites. Intercalated Polythiophene in V_2O_5 Xerogels

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During the last decade sol–gel-derived materials have attracted increasing attention from the chemical, materials science, and physics communities due to their demonstrated as well as potential value for the development of advanced structural[1] and electronic ceramics.[2] Vanadium oxide xerogels in particular are unique among sol–gel-derived materials[3] because they posses a porous layered structure with an interlayer distance of 11.55 Å[4] and they are capable of host–guest intercalation chemistry with a variety of species (i.e., alkali-metal ions,[5] alkylamines,[6] alcohols,[6] sulfoxides,[6] tetrathiafulvalene[7] (TTF), benzidine,[7] etc). The driving force for this intercalation chemistry depends on the guest species and can involve cation exchange, acid–base, or redox chemistry. $V_2O_5{\cdot}nH_2O$ xerogels (n ~ 1.6–2.0) are strongly oxidizing and amenable to redox intercalation chemistry. It is well-known that organic molecules such as aniline, pyrrole and thiophene yield, upon chemical or electrochemical oxidation, technologically

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† Michigan State University.

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(1) Hensch, L. L.; Ulrich, D. R. In *Science of Ceramic Chemical Processing*, and references therein; Wiley: New York, 1986.

(2) Brinkner, C. J., Clark, D. E., Ulrich, D. R., Eds. In *Better Ceramics Through Chemistry*; *MRS Symp. Proc.* **1988**, *121*, and references therein.

(3) (a) Aldebert, P.; Baffier, N.; Gharbi, N.; Livage, J. *Mater. Res. Bull.* **1981**, *16*, 669–676. (b) Legendre, J.-J.; Livage, J. *J. Colloid Interface Sci.* **1982**, *94*, 75–83. (c) Legendre, J. J.; Aldebert, P.; Baffier, N.; Livage, J. *J. Colloid Interface Sci.* **1982**, *94*, 84–89. (d) Aldebert, P.; Haesslin, H. W.; Baffier, N.; Livage, J. *J. Colloid Interface Sci.* **1983**, *98*, 478–483. (e) Gharbi, N.; Sanchez, C.; Livage, J.; Lemerle, J.; Nejem, L.; Lefebvre, J. *Inorg. Chem.* **1982**, *21*, 2758–2765.

(4) (a) $V_2O_5{\cdot}xH_2O$ xerogels are prepared by drying (at ambient temperature) gels formed from the polycondensation of vanadic acid. The dried gels (xerogels) possess a turbostratic structure composed of stacked but randomly oriented vanadium oxide layers. (b) Lemerle, J.; Nejem, L.; Lefebvre, J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 17–20.

(5) Lemordant, D.; Bouhaouss, A.; Aldebert, P.; Baffier, N. *Mater. Res. Bull.* **1986**, *21*, 273–280.

(6) (a) Aldebert, P.; Baffier, N.; Legendre, J.-J.; Livage, J. *Rev. Chim. Mineral.* **1982**, *19*, 485–495. (b) Lemordant, D.; Bouhaouss, A.; Aldebert, P.; Baffier, N. *J. Chim. Phys.* **1986**, *83*, 105–113. (c) Aldebert, P.; Baffier, N.; Gharbi, N.; Livage, J. *Mater. Res. Bull.* **1981**, *16*, 949–955. (d) Ruitz-Hitzky, E.; Casal, B. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1597–1604.

(7) (d) Van Damme, H.; Letellier, M.; Tinet, D.; Kihal, B.; Erre, R. *Mater. Res. Bull.* **1984**, *19*, 1635–1642. (e) Masbah, H.; Tinet, D.; Crespin, M.; Erre, R.; Setton, R.; Van Damme, H. *J. Chem. Soc., Chem. Commun.* **1985**, 935–936.

0897-4756/90/2802-0222$02.50/0