were found. The growing face principally investigated was that perpendicular to the crystallographic *c*-axis (0001). While this face does appear in some natural crystals, it is not predominant in natural corundum and might therefore be expected to be fast growing. However, under hydrothermal conditions it has been found to be quite persistent, (0001) seeds kept that face even when grown to considerable thickness. Microscopic examination of spontaneously nucleated hydrothermal corundum crystals showed them to be hexagonal platelets whose (0001) faces persisted even when quite thick. These spontaneously nucleated crystals were bounded almost always by (0001) and (11$\bar{2}$0) with only the occasional appearance of other faces. One might therefore deduce that under hydrothermal conditions (0001) is not an especially fast-growing face. Indeed preliminary indications are that several other faces are faster growing. When cylindrical plates whose ends were (0001) were used as seeds, (11$\bar{2}$0) faces were formed quickly but (0001) persisted.

Crystals generally were grown on wafers with either the *c*-axis normal or inclined 60° to the plane of the wafer. Increases in dimensions of about 0.25 in. in the *c* and 0.30 in. in the *a* direction have been achieved. Crystals with natural faces formed as large as $^3/_4''$ in the *a* and 0.40 in. in the *c* direction have been prepared. Increases in weight of over 200% have been achieved.

Green crystals containing iron have been grown by carrying on the crystallization in the welded liner directly and colorless crystals which were essentially pure have been prepared by the use of the silver tube.

Crystals doped with chromium (synthetic ruby) have been prepared. Concentrations of $Na_2Cr_2O_7 \cdot 3H_2O$ of about 0.10 g./l. caused about 1% chromium by weight to be included in the crystal. The resultant crystals were blood red in color.

Further studies of the conditions for crystallization, the solubility and phase equilibria relationships, and the properties of the grown sapphire are in progress.

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[CONTRIBUTION FROM MERCK SHARP & DOHME RESEARCH LABORATORIES DIVISION, MERCK & CO., INC.]

Synthesis of Selenides and Tellurides. I. The Reduction of Selenites by Hydrazine

BY WALTER C. BENZING, JOHN B. CONN, JAMES V. MAGEE AND EDWARD J. SHEEHAN

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Aqueous hydrazine of strength sufficient to dissolve selenium reduces metallic selenites to selenides, provided that the product is insoluble in the reaction medium. The selenides of cadmium, copper(I), copper(II), lead(II), mercury(II) and zinc have been produced in excellent yields *via* this reaction. In the cases of zinc and cadmium, isolable hydrazino selenide complexes of formula $MSe \cdot N_2H_4$ are formed as intermediates.

The high interest in the semi-conducting properties of selenides and tellurides has made desirable the development of safe and efficient methods for their production. In particular, such methods should be capable of yielding high-purity products, both as regards compositional ratio and trace contaminants without recourse to lengthy and cumbersome procedures; further, in view of the serious health hazard involved in the handling of selenium and tellurium compounds, the processes should preferably avoid the use of volatile materials. It is the purpose of this and subsequent papers to describe processes designed to meet these conditions.

Previously described methods for preparing selenides comprise: (1) union of the elements at elevated temperature; (2) reduction of selenites and selenates by hydrogen or ammonia at elevated temperature; (3) metathesis of metal salts with hydrogen, ammonium or alkali selenides; (4) reduction of selenium in alkaline solution or selenosulfate by means of dithionite[1,2]; (5) and in the special case of cadmium selenide, by decomposition of selenosulfate ion in presence of cadmium ion.[3]

Hovorka[4] studied the reduction of alkali selenites by means of aqueous hydrazine as being of possible analytical interest, but found that the product is a mixture of selenide and selenium (*i.e.*, polyselenide). This proves likewise to be the case when a water-insoluble selenite is digested with dilute hydrazine: selenium is precipitated and reduction ceases at that point. On the other hand, the solubility of selenium increases with hydrazine concentration by way of the equilibrium[5]

$$6N_2H_4 + 3H_2O + (2x + 1)Se \rightleftarrows 6N_2H_5^+ + 2Se_x^= + SeO_3^=$$

and use can be made of this property to bring about complete reduction.

Addition of solid zinc selenite to a 4–10 fold excess of commercial hydrazine hydrate pre-heated to about 80°, results in a vigorous evolution of nitrogen and heat, and formation of a white to peach-colored insoluble solid. This substance was identified as the novel complex hydrazinozinc selenide, $ZnSe \cdot N_2H_4$

$$2ZnSeO_3 + 5N_2H_4 \longrightarrow 2ZnSe \cdot N_2H_4 + 6H_2O + 3N_2$$

It forms dense, acicular crystals which are stable

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(1) L. Tschugaeff and W. Chlopin, *Ber.*, **47**, 1269 (1914).

(2) S. M. Thomsen, U. S. Pat. 2,534,562 (to Radio Corporation of America), Dec. 19, 1950.

(3) N. E. Gordon and E. C. Pitzer, *Ind. Eng. Chem., Anal. Ed.*, **10**, 68 (1938).

(4) V. Hovorka, *Chem. Listy*, **27**, 25, 49 (1933).

(5) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie, Weinheim, 1952, Vol. 10A, p. 249.

in air at room temperature, but catch fire when ignited. Gentle heating under inert gas brings about conversion to zinc selenide with the calculated loss in weight. The product obtained at 500° commonly turns out to be the meta-stable hexagonal modification; at 800°, this goes over to the stable cubic form. Degradation of the hydrazine complex is likewise accomplished by digestion with dilute acid, preferably acetic. It is interesting that abstraction of hydrazine occurs without dissolution of the solid; the (now yellow) product retains the external crystal form of the complex, but is found by X-ray diffraction to be substantially amorphous. This fortunate circumstance renders the zinc selenide air-stable at room temperature in absence of light.

The hydrazine reduction of cadmium selenite is characterized by an induction period, during which the color of the suspension changes from white to orange, with gentle nitrogen evolution. The color then passes through red and maroon, with acceleration in gassing, to eventual brown. Care must be taken not to add cadmium selenite too rapidly in the early stage, lest the reaction later become uncontrollable. The induction period is associated with the primary formation of difficultly soluble hydrazino cadmium selenite, which later dissolves with increasing rate as the temperature rises. It was found that the presence of acetate ion limits the induction period, probably by increasing the solubility of hydrazinocadmium selenite; in fact, the addition of acetate is beneficial in all reductions of selenites by hydrazine.

Product isolated at the orange to red stage lost weight on ignition or acid treatment to about that required by hydrazinocadmium selenide; at the maroon stage, less; and at the brown, little or none. The orange solid was amorphous by X-ray diffraction, while the darker products exhibited reflections of cadmium selenide. The evidence thus points to formation of hydrazinocadmium selenide as an unstable intermediate in the reduction. The solids at all stages are bulky and finely divided, and the reaction mixture can become so thick as dangerously to inhibit gas escape if the hydrazine is too concentrated. Routine dilution of 85% hydrazine hydrate with half its volume of water minimizes the difficulty.

There is further advantage in adding zinc and cadmium selenites in solution as the respective ammine complexes; not only does such procedure assist control of the reaction, but also copper and silver doping agents can be incorporated in desired amount.

The reduction of lead, mercury(II) and copper(II) selenites is carried out similarly; no evidence was adduced for the existence of any hydrazino selenide intermediate. Lead and mercury(II) selenides so obtained are highly crystalline. Copper(I) selenide is prepared by adding an ammoniacal solution of 1 mole copper(II) acetate and 0.5 mole selenious acid to hydrazine

$$2Cu(NH_3)_4^{++} + SeO_3^{=} + 2N_2H_4 \longrightarrow Cu_2Se + 2NH_4^+ + 6NH_3 + 3H_2O + 2N_2$$

Cobalt(II) selenite, as a representative of the transition metals, underwent reduction with extreme violence, the eruption of gas continuing until the flask residue was nearly dry (without, however, hurling any solid out). The black product contained both cobalt and selenium, but proved to be pyrophoric. It was concluded that the (presumably cobalt selenide) product catalyzes the spontaneous decomposition of hydrazine.

The selenites of magnesium, calcium, strontium and barium fail to react with hydrazine at all in absence of acetate; when acetate is added, reduction sets in, but the solution assumes the red color of polyselenide and no solid separates. This parallels the observation of Hovorka (ref. 4); the evidence indicates that to achieve complete reduction, the selenide or its hydrazino complex must be insoluble in the reaction medium.

Tellurides cannot be prepared by reduction of tellurites in the manner here described, since tellurium is insoluble in hydrazine. Alternative approaches will be discussed in subsequent publications.

Experimental

Selenites.—These were prepared by mixing together equivalent amounts of pure metal acetate and selenious acid solutions, or, where applicable, by passing ammonia gas into a mixture of metal sulfate and selenious acid solutions to *p*H 8. The crystalline solids were washed thoroughly with deionized water and dried at 80°.

Hydrazinozinc Selenide.—A 12-l., 3-necked flask was mounted on the steam cone and fitted with a sealed stirrer, reflux condenser, nitrogen inlet tube and a solids feeder comprising a covered glass hopper and motor-driven Teflon worm. The flask was charged with 5400 ml. of redistilled 85% hydrazine hydrate and 180 ml. of saturated aqueous zinc acetate solution. The stirrer was started, the reaction mixture was heated to 80–85°, and zinc selenite was admitted *via* the feeder. When reaction was well under way, as indicated by lively gas evolution and refluxing, steam heating was discontinued, and the feeder regulated so as to admit a total of 2304 g. (12 moles) of zinc selenite over a period of 2.75 hours. When gas evolution slackened at the end, nitrogen was admitted, and zinc selenite clinging to the feeder and flask wall was dislodged into the reaction mixture, with the aid of deionized water. Flask and contents were allowed to cool under nitrogen. The peach-colored solid was collected on a filter, washed with deionized water and methanol, and allowed to dry at room temperature in the cloth-covered funnel; yield 1992 g. (94%).

Anal. Calcd. for $ZnSe \cdot N_2H_4$: N, 15.90; ignition loss, 18.2. Found: N, 16.25; ignition loss, 18.5.

The X-ray diffraction pattern was obtained on a finely-ground flat specimen, using Norelco wide-range Geiger counter equipment, and nickel-filtered copper radiation. Table I lists the interplanar spacings (Å.) and associated relative intensities.

Table I

Hydrazinozinc Selenide X-Ray Diffraction Data

8.34(31); 7.19(100); 4.80(7); 4.61(8); 3.89(<2); 3.65_0(7); 3.57_0(9); 3.32_0(16); 3.22_5(53); 3.17_0(16); 3.12_0(18); 3.01_0(2); 2.96_0(6); 2.93_5(12); 2.89_0(6); 2.840(9); 2.763(<2); 2.598(3); 2.549(<2); 2.468(3); 2.405(2); 2.390(6); (2.295,2.281)(5); 2.226(2); 2.196(2); 2.166(3); 2.130(3); 2.098(2); 2.056(5); 1.996(3); (1.969,1.952)(9); 1.909(5); 1.878(7); 1.847(9); (1.837,1.815)(2); 1.799(5); 1.788(–); 1.756(–); 1.744(–); 1.738(–).

Zinc Selenide.—The product from the previous step was added to a mixture of 3 l. of redistilled glacial acetic acid and 3 l. of deionized water in a 12-l. flask under nitrogen and dim light. The continuously stirred suspension was heated on the steam cone for 2 hours, during which time the solid became yellow. After the suspension had cooled to room temperature, it was filtered with suction (dim light), washed free from acid with deionized water, then with methanol, and dried overnight in a 100° oven under nitrogen atmosphere. The oven was allowed to cool to room temperature before opening. The solid weighed 1762 g.; ignition loss under nitrogen was 8.1%, giving a corrected yield of 1619 g. (93.5%, based on zinc selenite).

Anal. Calcd. for ZnSe: Zn, 45.4; Se, 54.6. Found (after ignition): Zn, 45.9; Se, 54.2.

Zinc Selenide from Ammine Selenite Complex.—Wet zinc selenite filter cake prepared from 9 moles each of zinc acetate and selenious acid was suspended in 1150 ml. of deionized water, and ammonia gas was passed in to complete dissolution. This was added to 4 l. of 85% hydrazine hydrate and 50 g. of zinc acetate over 1.5 hours under conditions as previously described. The hydrazino selenide was decomposed in acetic acid; yield of zinc selenide, corrected for ignition loss, 1297 g. (quantitative).

Hydrazinocadmium Selenide.—To 150 ml. of 85% hydrazine hydrate, warmed on the steam cone, was added 23.94 g. (0.1 mole) of cadmium selenite; the originally white suspension was converted into bright orange, with a gradually accelerating evolution of nitrogen. The bulky, orange solid was collected on a filter, washed with deionized water and methanol, and dried; yield 21.50 g. (96.3% as $CdSe \cdot N_2H_4$).

Anal. Calcd. for $CdSe \cdot N_2H_4$: N, 12.56; ignition loss, 14.2. Found: N, 12.71; ignition loss 16.7 (some sublimation was noticed). The hydrazino selenide was nearly amorphous as judged by X-ray diffraction.

Cadmium Selenide.—Cadmium selenite wet filter cake prepared from 15 moles of selenious acid, was added to 6.5 l. of deionized water containing 1575 g. of ammonium carbonate and dissolved by passing in ammonia gas. This solution was fed into 8 kg. of 85% hydrazine hydrate in a 22-l. flask under continuous agitation and maintenance of temperature at 85–100°. The color of the suspension rapidly passed through the orange and maroon stages to brown-black with vigorous evolution of nitrogen; operation was completed in 3.5 hours. When the mixture had cooled, the solid was collected upon Whatman No. 50 paper in a 32 cm. funnel, slurried with 50% acetic acid to destroy any remaining hydrazino cadmium selenide, then washed with deionized water and methanol, and dried at 120° under carbon dioxide; yield 2815 g. (98%, based on selenious acid).

Anal. Calcd. for CdSe: Cd, 58.7; Se, 41.3. Found: Cd, 58.2; Se, 41.2.

Lead(II) Selenide.—Lead(II) selenite (334 g., 1 mole) was added gradually to a stirred and pre-heated mixture of 450 ml. of 85% hydrazine hydrate, 200 ml. of water and 5 ml. of glacial acetic acid. Reduction was vigorous; the product weighed 280 g. (98%, as PbSe). The solid was black, graphitic in texture, and gave a sharp X-ray diffraction pattern characteristic of cubic lead selenide.

Anal. Calcd. for PbSe: Pb, 72.4; Se, 27.6. Found: Pb, 72.1; Se, 27.9.

Mercury(II) Selenide.—Reduction of mercury(II) selenite, as described above, was violent, and care had to be taken during the addition. From 236 g. (0.72 mole) of selenite, there was obtained 190 g. (94.5%) of crystalline mercury(II) selenide.

Anal. Calcd. for HgSe: Hg, 71.7; Se, 28.3. Found: Hg, 70.7; Se, 29.2.

Copper(II) Selenide.—From 0.76 mole of copper(II) selenite there was obtained 109 g. of copper(II) selenide (quantitative).

Anal. Calcd. for CuSe: Cu, 44.4; Se, 55.6. Found: Cu, 44.4; Se, 55.8.

Copper(I) Selenide.—A mixture of 1 mole of copper(II) acetate and 0.5 mole of selenious acid was treated with ammonia gas until all solid dissolved. This solution was run dropwise into preheated hydrazine reduction mixture as described above; yield 104 g., ignition loss, 5.0% (95% as Cu_2Se).

Anal. Calcd. for Cu_2Se: Cu, 61.3; Se, 38.7. Found (after ignition): Cu, 60.7; Se, 39.3.

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RAHWAY, N. J.

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Perchloryl Fluoride. Vapor Pressure, Heat Capacity, Heats of Fusion and Vaporization Failure of the Crystal to Distinguish O and F[1]

BY J. K. KOEHLER AND W. F. GIAUQUE

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The heat capacity of perchloryl fluoride has been measured from 15 to 225°K. The heat of fusion was found to be 916.3 cal. mole^{-1} at the melting point which was determined as 125.41°K. The heat of vaporization was determined calorimetrically to be 4619 cal. mole^{-1} at the boiling point, 226.48°K. The $\int_0^{\text{b.p.}} C_p \, d \ln T$ gave 60.17 cal. deg.$^{-1}$ mole^{-1} for the ideal gas at 226.48°K. This is 2.42 cal. deg.$^{-1}$ mole^{-1} less than the entropy value 62.59 cal. deg.$^{-1}$ mole^{-1} based on gas molecular data at this temperature. This is in accordance with expectations that the crystal would largely fail to distinguish between O and F, which would lead to a maximum discrepancy of $R \ln 4 = 2.75$ cal. deg.$^{-1}$ mole^{-1}. The vapor pressure was measured and the data are represented by the equation $\log_{10} P(\text{int. cm.}) = -1652.37/T - 8.62625 \log_{10} T + 0.0046098T + 28.44780$.

In several previous investigations in this Laboratory $\int_0^T C_p \, d \ln T$ has been short of the known value of the entropy at ordinary temperatures by approximately $R \ln 2$. This has occurred in cases where molecules have contained carbon, oxygen and nitrogen atoms in positions which would otherwise be equivalent. Crystals do not distinguish, to any appreciable extent, between the several isotopes of an element and Clayton and Giauque[2] suggested that when substances solidify, crystals may also fail to order their systems with respect to different elements of similar size which occupy positions which would otherwise be nearly symmetrically equivalent. They explained the entropy discrepancy in their work on carbon monoxide in this way and predicted that it would occur in other cases when somewhat similar atoms or groups of atoms occupied two or more equivalent positions without producing much asymmetry.

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[1] This work was supported in part by the National Science Foundation and by the Office of Naval Research United States Navy. The U. S. Government may reproduce this article.

[2] J. O. Clayton and W. F. Giauque, THIS JOURNAL, **54**, 2610 (1932).