Reaction Chemistry of Crystalline Allotropes of Germania

Lawrence Seibles, James W. Mitchell, and Lawrence D. Blitzer

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Chemical reactions potentially useful for converting intractable allotropes of germania (aged hexagonal and tetragonal forms) into reactive products are investigated. The effectiveness of reactions in aqueous solutions under basic, basic–reductive, acidic–oxidative, and acidic–reductive conditions is reported in terms of germania solubilization. Solubility versus time of reaction at elevated temperatures is reported for the most effective medium, 2.5M NaOH. For six flux media, fusion reactions and respective temperatures are reported with the percentage of germania solubilized from the fused melt. Additionally, the crystalline germania materials are characterized by infrared and differential thermal analyses. Chemical procedures compatible with batch or continuous processing methods are discussed. [Key words: germania, crystal chemistry, synthesis, processing, and solubility.]

A MPLE supplies of germanium (Ge) raw materials are critical for several technologies. Infrared and radiation detectors and optical waveguide fiber manufacturing depend on Ge chemicals. Demands have increased over the past few years. As indicated by a recent examination of Ge supply–demand influences on prices, the cost of germanium tetrachloride ($GeCl_4$) has increased sharply as supplies of raw materials have been restricted, particularly within the United States.[1] Although Ge-bearing ores are plentiful in the Soviet Union and in Africa, North American mines of major Ge-containing ores are sparse. However, a vast potential U.S. reserve exists in the form of coal, from which Ge may be recovered from certain fly ashes containing several hundred ppm of the element. Currently, domestic Ge is obtained predominantly as a byproduct of Zn mining.

During conventional processing of Ge ores, the element is recovered by treating the raw material with concentrated HCl-containing chlorine. The resulting $GeCl_4$ is recovered by distillation and is

often hydrolyzed subsequently to precipitate germania (GeO_2). From GeO_2, the metal is produced by reduction and may be purified eventually by zone refining. As originally precipitated, hexagonal germania (h-GeO_2) may be redissolved quite readily in aqueous media (acid and base) and may easily be converted to $GeCl_4$. However, the reactivity, solubility, and rate of dissolution of the h-GeO_2 depends on several factors, including thermal treatment, dehydration, and impurity content.[2] With increased extent of dehydration or aging, the solid progressively becomes more sluggish in its solubilization with reagent chemicals. The tetragonal allotrope (t-GeO_2) is particularly chemically intractable and does not react even with aqueous HF or HCl. This very stable form of GeO_2 is generally produced under conditions of instability of the vitreous and hexagonal materials (hydrothermal, mineralizing catalysts, pressure) and upon slow transformation of the hexagonal solid on long-term aging. Because of its low reactivity, t-GeO_2 is not ordinarily sought as a precursor material for producing Ge compounds. However, t-GeO_2 films can be expected to import stabilizing and masking properties to surfaces; thus, it is generally investigated for device applications and technology.

Prior to 1980, it is reported that most of the domestic byproduct Ge concentrates from metal mining were discarded over the years because of lack of demand.[1] Apparently, Ge concentrates from large-scale African mining have also been discarded or stored near the mining location. These residues contain several hundred ppm of Ge. During processing to refine such ores, particularly to obtain Zn, h-GeO_2 and smaller quantities of t-GeO_2 can be precipitated. Once isolated and dried, these solid, high Ge-containing materials are not generally processable by the conventional methods commonly used either to recover Ge from natural ores or to produce other Ge compounds.

Needs for $GeCl_4$ for optical waveguide fiber manufacturing are expected to remain relativley high. To meet these demands for Ge, the purchasing and reprocessing of large quantities of chemically intractable GeO_2 might prove essential. The objective of this study is to investigate the most direct and economically feasible procedures for converting GeO_2 into chemically reactive products useful as Ge raw materials. Results of experiments on h-GeO_2 subjected to long-term aging and on t-GeO_2 prepared in our laboratory are

reported. Chemical procedures compatible with batch or continuous chemical engineering production-scale processing methods are discussed.

EXPERIMENTAL PROCEDURE

Dissolution

The solubilization of GeO_2 in various reagent solutions was examined under accelerated conditions of high temperature and pressure produced within a Teflon* pressure bomb apparatus.[3] Reaction mixtures of concentrated HNO_3–49% HF (1:4), 50% hypophosphorous acid–6M HCl (5:1), or 30% H_2O_2–6M HCl (1:2) were prepared. Samples (0.25 to 1.0 g) of GeO_2 were transferred into the bomb apparatus and covered with 10 mL of the reaction mixture. The bomb apparatus was heated within an oven for periods of up to 24 h at 180°C. h-GeO_2 (0.25 g) was reacted with 12.5 mL of 2.5M NaOH, an amount capable of dissolving 4 times the quantity of GeO_2 being tested. Samples within several bomb apparatus were removed at various time periods to determine the minimum solubilization time. Alternatively 1-g samples of GeO_2 were submerged under 50 mL of 2.5M NaOH within a 100-mL covered Teflon (TFE) beaker and heated continuously at 100°C. A 0.5-mL aliquot of the solution was removed at various time intervals and analyzed by atomic absorption spectroscopy. In a similar manner, 0.5-g samples of h-GeO_2, preheated for 30 min at 1100°C, were shaken in separate funnels with 100 mL of 2.5M NaOH and with 100 mL of 0.6M oxalic acid.

Fusion

GeO_2 (0.25 to 1.0 g) was fused with 7 times the weight of each flux reagent. In each case, approximately one-half of the flux was placed on the bottom of a Ni or quartz crucible, the GeO_2 was added next, and finally covered with the remaining portion of flux. The crucible was then held with tongs within an air–gas flame, and the materials fused carefully until a fluid melt was formed. The fused sample was subsequently heated with small volumes of 2.5M NaOH until either no residue remained within the crucible or no further solubilization was evident. To prevent reprecipitation of the solubilized Ge species resulting from dissolving the melt in small, heated portions of 2.5M NaOH, it was necessary to add the small concentrated solution to a larger volume (75 mL) or 2.5M NaOH. This dilution prevented precipitation from the otherwise saturated

small volume sample. Conditions for fusion with various reagents (sodium peroxide, sodium carbonate, sodium oxalate, sodium hypophosphite, sodium hydroxide, and sodium formate) were compared by qualitatively examining fusion times, fusion temperature, ease and completeness of the solubilization of the melt and by quantitatively analyzing the resulting solution for Ge.

Tetragonal Germania

The procedure of Faktor and Carasso[4] was used to obtain a batch quantity ($\approx$20 g) of pure t-GeO$_2$. The catalyst used was LiGeO$_2$ prepared by heating to 1250°C equal molar quantities of t-GeO$_2$ and LiCo$_3$ contained in a Pt crucible. h-GeO$_2$ containing approximately 0.1 wt% of LiGeO$_2$ was heated at 900°C for >24 h in a covered Pt crucible. A control sample containing no catalyst was also heated under similar conditions, but showed no reaction. Infrared spectra (KBr pellets) and differential thermograms (25° to 1200°C, 20°C/min in air) were obtained for the tetragonal product, the original hexagonal sample, and an ultrapure (99.99+%) reference source of h-GeO$_2$ obtained commercially.[†]

RESULTS AND DISCUSSION

The solid modifications of GeO$_2$ include an amorphous or vitreous form and two crystalline allotropes, hexagonal (quartz-type) and tetragonal (rutile-type). These modifications are readily distinguishable by their infrared spectra and from X-ray powder analysis. The stable, tetragonal form is chemically intractable, but does not ordinarily form, except under conditions of instability of the more reactive hexagonal allotrope. Reactions producing GeO$_2$ under conditions thermodynamically compatible with all forms invariably yield the vitreous or hexagonal forms of GeO$_2$ the oxide. Unexpectedly, GeO$_2$ was presumed to be of the hexagonal variety and to be commercially available in bulk quantities showed vary sluggish chemical reactivity. This GeO$_2$ was, therefore, examined by several techniques. Infrared spectra of the commercial product and the tetragonal material prepared in this work are shown in Fig. 1, with a spectrum of an ultrapure (99.99+%) h-GeO$_3$ standard. These data confirmed the purchased material to be of the hexagonal variety, with few discernible differences detected in the spectra of the former and the hexagonal standard. Emission spectrographic analysis of the hexagonal sample showed a material of better than 99% purity, with detectable impurities (Ag, Ca, Mg, Cu, and Fe) found at the 10 ppm level or below. However, Si was found to be present at about 100 ppm. Qualitative X-ray fluorescence analysis also did not detect the presence of S.

Differential thermograms for the three oxide samples are presented in Fig. 2. Substantial differences were observed in the thermal behavior of the purchased hexagonal material and the hexagonal standard. The tetragonal sample exhibited a low-temperature endotherm (80° to 100°C), presumably reflecting release of adsorbed moisture, and a large endotherm at 1030° to 1050°C, corresponding to rapid conversion to the hexagonal structure. This latter transition is reported to occur at 1030°C.[4] The endotherm occurring around 1100°C is due to melting of the oxide.

The hexagonal standard exhibited a specific exothermic change in the 600° to 700°C region that was not observed in any of the other samples. This effect, we suspect, is due to residual water of hydration which is only completely removed from the oxide above 800°C, as possibly indicated by the weak endotherm in the 840° to 900°C region. The lower-temperature endotherm could thus be explained by a hydrothermal conversion of some hexagonal material to the tetragonal form which is more stable by approximately 6 kcal/mol.[4]

In addition to the general background features and melting transition exhibited by the other samples, the commercial hexagonal material showed only a weak endotherm occurring in the 1050° to 1070°C region, corresponding to the tetragonal-to-hexagonal transformation. These results confirmed that this material was extremely dry and contained small amounts of the tetragonal oxide, a consequence, perhaps of long-term aging, resulting in its observed sluggish reactivity and poor solubilization characteristics.

Reactions in Acidic Media

Samples of the h- and t-GeO$_2$ were exposed to various solutions having high chemical potential for destroying the GeO$_2$ matrix. The solution chemistry of the hexagonal material was examined first in detail. Only the most effective reactions were then investigated for the tetragonal compound. Accelerated conditions of ele-
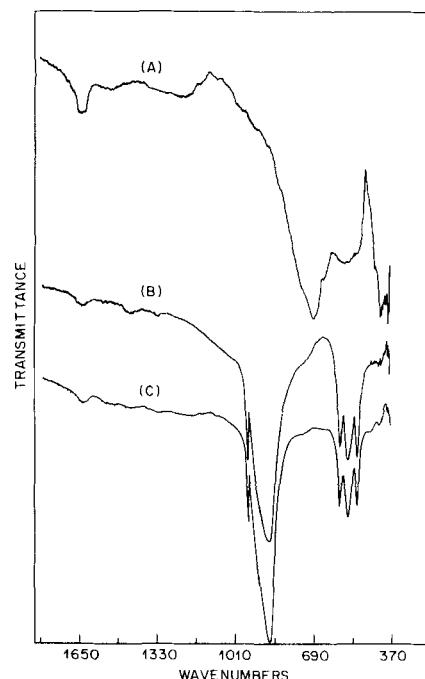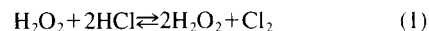

Fig. 1. Infrared spectra of crystalline allotropes of germania: (A) tetragonal, (B) hexagonal, and (C) commercial solid.

vated pressure and high temperature were examined by using Teflon (TFE) pressure bomb vessels. Strong oxidizing agents in combination with strong complexing anions for Ge were examined. H$_2$O$_2$–HCl reacts according to the equation

$$H_2O_2 + 2HCl \rightleftharpoons 2H_2O_2 + Cl_2 \qquad (1)$$

to produce Cl$_2$ (in the presence of excess HCl). Exposure of h-GeO$_2$ to this medium produced partial solubilization, as indicated by the results in Table I. Thus, formation of the hexachlorogermanic acid via the reaction

$$GeO_2 + 6HCl \rightleftharpoons H_2GeCl_6 + 2H_2O \qquad (2)$$
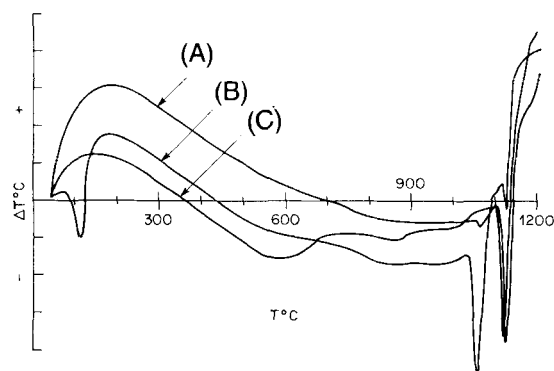
and/or complexation by H$_2$O$_2$ according to the reaction

Fig. 2. Different thermograms of crystalline allotropes of germania, 25° to 1150°C at 20°C/min in air: (A) tetragonal, (B) hexagonal, and (C) commercial solid.

Table I. Solubilization Germania in Reagent Solutions

Reagent	Weight of GeO₂ (g)	Volume of reagent (mL)	Exposure time (L)	Solubilization (%)	[Ge] (mg/mL)
0.1M NaH₂PO₂ in 2.5N NaOH	0.25	15	20	100	11.2
	0.20*	10*	20*	100*	14.2*
H₃SO₃ (6% SO₂)	0.25	10	7	46	7.6
2.5N NaOH	0.25	12	7	100	13.5
	0.20	10*	7*	100*	14.1
6M HCl–30% H₂O₂ (2:1)	0.25	10	17	62	10.4
50% H₃PO₂–6M HCl (5:1)	0.25	9	18	90–100	17.3
49% HF–16M HNO₃ (4:1)	0.25	10	18	90–100	17.7

*Prepared tetragonal material, all others were purchased hexagonal material identified by infrared spectroscopy as the hexagonal intermediate.

Table II. Solubility of *h*-GeO₂ in 2.5N NaOH vs Time at 100°C (mg of Ge/mL)

Sample	1 h	2 h	4 h	6 h
1*	9.1	14.6	14.6	17.3
2†	13.1	13.1	12.0	

*Original sample. †Preheated for 30 min at 1100°C.

$$GeO_2 + 2H_2O_2 \rightleftarrows O_2Ge(-OH)_4 \qquad (3)$$
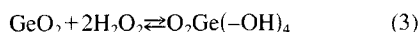
provide measurable solubilization in the presence of Cl_2 and high temperature (180°C). Upon reacting with mixtures of hydrofluoric and nitric acids, *h*-GeO₂ was decomposed substantially according to

$$GeO_2(s) + 6HF \rightleftarrows H_2GeF_6 + 2H_2O \qquad (4)$$

Under reducing conditions, the *h*-GeO₂ matrix is strongly attacked chemically in an acid medium. For example, the reactions

$$GeO_2(s) + H_3PO_2 \rightleftarrows GeHPO_3(s) + H_2O \qquad (5)$$

$$GeHPO_3(s) + 3HCl \rightleftarrows HGeCl_3 + H_3PO_3 \qquad (6)$$
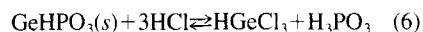
were almost complete after 18 h under the conditions investigated. Chemical attack is dependent on the ratio of the concentration of the reducing acid to that of HCl.

The reaction with sulfurous acid (6% SO₂)

$$GeO_2 + H_2SO_3 \rightleftarrows GeSO_4 + H_2O, \qquad (7)$$

failed to dissolve this reasonably intractable form of the hexagonal solid. Maximum solubility was 7.6 g/L of Ge.

Reactions in Basic Media

Previous studies indicated that a maximum in the solubility of *h*-GeO₂ occurs in 2.5M NaOH.[2] Because chemical attack in solutions on the tetragonal form leads to

the precursor of the hexagonal form, solubilization studies of both materials have been confined to scrutiny of 2.5M reagent.

At room temperature, the reaction

$$GeO_2 + 2OH \rightleftarrows GeO_3^{2-} + H_2O \qquad (8)$$
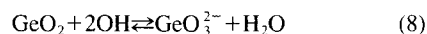
is quite slow, as indicated by the observation that *h*-GeO₂ only dissolved to the extent of 0.44 mg/mL in 2.5M NaOH and to 0.084 mg/mL in 0.65M oxalic acid. This limited solubility of our commercially procured material is contrasted with the solubility of the freshly prepared hexagonal *h*-GeO₂ in 2.5M NaOH (80 mg/mL) and in 0.6M oxalic acid (≥20 mg/mL). Results of the solubilization of *h*-GeO₂ in the various reagents studies are given in Table I.
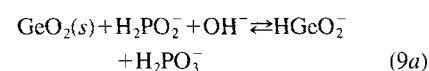
Under well-controlled conditions, the solubility of *h*-GeO₂ was determined in 2.5M NaOH at 100°C. In a covered Teflon (TFE) beaker, 1 of the material submersed in 50 mL of 2.5M NaOH was heated in a furnace. The solubility of the matrix was followed by analyzing aliquots of the solutions versus time of heating. The results (Table II) confirm the resistance of the material to chemical attack upon prolonged conventional heating with reagent solutions. However, significant solubilization is achieved within 6 h.

Under the standard conditions of this study of the dissolution of GeO₂ within a Teflon pressure vessel (180°C for 24 h), *h*- and *t*-GeO₂ were dissolved completely in a quantity of 2.5M NaOH sufficient to accommodate 4 times the treated amount. The formation of the GeO_3^{2-} ion via Eq. (8) is therefore quite effective for solubilization under accelerated conditions. Treatment and observation of samples for periods less than 24 h (1, 3, 5, 6, 7, 12, and 19 h) indicated complete dissolution of both the

hexagonal and the tetragonal form after 7 h in a Teflon pressure vessel.

The more vigorous chemical attack induced by 2.5M NaOH on the GeO₂ than that resulting from other tested chemicals makes this the reagent of choice for converting the purchased product into a form compatible with further chemical processing. Large column beds of the solid heated to 100°C could be leached continuously with 2.5M NaOH.

Accelerating the chemical dissolution of the material via 2.5M NaOH mixture containing reducing agents was achieved. Samples of the hexagonal oxide were treated with 0.1M NaH₂PO₂ in 2.5M NaOH in pressure vessels for 7 h. The resulting solution with suspended, finely divided, clear, crystalline particles, yielded a gelatinous, milky precipitate upon neutralization with HCl. With additional acidification, the precipitate redissolved completely to form a particle-free, clear solution. The chemical reactions corresponding to these observations are

$$GeO_2(s) + H_2PO_2^- + OH^- \rightleftarrows HGeO_2^-$$
$$+ H_2PO_3^- \qquad (9a)$$

$$HGeO_2^- + H^+ \rightleftarrows Ge(OH)_2 \qquad (9b)$$

$$HGeO_2^- + H_2PO_2^- \rightleftarrows GeHPO_3 + 2OH^- \qquad (10a)$$

$$Ge(OH)_2 + 3HCl \rightleftarrows HGeCl_3 + 2H_2O \qquad (10b)$$

$$GeHPO_3 + 3HCl \rightleftarrows HGeCl_3 + H_3PO_3 \qquad (11)$$

Treatments of *h*-GeO₂ in this medium for periods as short as 3 h produced a colloidal suspension that was completely solubilized upon acidifying the solution with HCl. The tetragonal sample was solubilized completely after 7 h in the same reagent. Percentage solubilizations of 0.2 g of *t*-GeO₂ in 10 mL of 0.1M H₂PO₂–2.5M NaOH versus time were 62.7% in 3.25 h, 91% in 6.25 h, and 100% in 19.5 h.

In solutions of 2.5M NaOH alone, GeO₂ is solubilized completely as the GeO_3^{2-} ion, whereas basic solutions with hypophosphite generate the divalent species shown in Eq. (10a). The solubilities of these species in 2.5M NaOH are lower than that of the *t*-GeO₂ anion. Thus, the advantage of rapid dissolution of GeO₂ using reducing agents in basic media may be partially offset by the lower solubility of the divalent Ge species formed. However, subsequent dissolution–oxidation of the di-

Table III. Flux Materials Reacted with *h*-GeO₂

Flux	Weight of GeO₂ (mg)	Solubility of fused melt	Melting temperature of flux (°C)	Ge solubilized (%)
Na₂O₂	1000	Completely	460	92
*	249*	Completely*	460*	100*
Na₂CO₃	1000	Completely	851*	102
Na₂C₂O₄	500	Partially	250–270	89
NaCOOH	500	Partially	253	100
NaH₂PO₂	500	Partially	253	100
NaOH	500	Completely	318	92
*	232*	Completely*	318*	98*

*Tetragonal GeO₂ treated; all other data refer to commercial *h*-GeO₂.

valent compounds in 6.0M HCl–Cl$_2$ or 6.0M HCl–3% H$_2$O$_2$ occurs readily. From such solutions, chemically reactive GeO$_2$ could be precipitated by optimum adjustment of the pH. After removal of most of the supernatant fluid, direct treatment of the GeO$_2$ suspension with concentrated HCl containing excess Cl$_2$ is suitable for producing GeCl$_4$ by the conventional HCl distillation process.

Fused Solid Reactions

Destruction of intractable solid matrices by fusion to convert the material into easily solubilized products is a basic approach to sample treatment prior to chemical analysis. Although reactions of melts at elevated temperature have several inconveniences in comparison with dissolution with reactive liquid reagents, the significant advantage of rapid conversion to solubilizable products can be obtained. Consequently, the most suitable fluxing agents for GeO$_2$ were examined. Such an approach to the processing of GeO$_2$ at reasonably low temperature (<500°C) would be considered a simple and inexpensive operation in comparison with conventional smelting processes. Fluxes reported in Table III were evaluated and are discussed subsequently. Fusion with Na$_2$O$_2$ according to the reaction

$$GeO_2 + Na_2O_2 \rightleftharpoons Na_2GeO_3 + \tfrac{1}{2}O_2 \qquad (12)$$
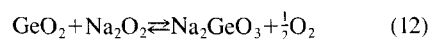
proceeds quickly for both the hexagonal and tetragonal solid. After some initial frothing due to oxygen evolution, a dark but clearly fluid melt is formed. After solidification, the gray melt was dissolved completely by heating with several volumes of 2.5M NaOH. A small amount of a flocculent precipitate was removed from the resulting solution by filtration and was shown by X-ray fluorescence to contain predominantly Ni and traces of Ge. The presence of Ni(OH)$_2$ due to contamination by the crucible is evident. Fusion in quartz crucibles completely eliminated this precipitate and also prevented darkening of the melt. Attempts to dissolve the melt directly into concentrated HCl are accompanied by the expected copious precipitation of NaCl.

With Na$_2$CO$_3$, more extensive heating over a considerably longer period than observed with Na$_2$O$_2$ was required to induce the fusion process. Considerable

frothing due to CO$_2$ evolution occurred also. The reaction

$$GeO_2 + Na_2CO_3 \rightleftharpoons Na_2GeO_3 + CO_2 \qquad (13)$$

is evident for the melt. Again the fused material was dissolved completely by heating with small volumes of 2.5M NaOH. Fusion of h- and t-GeO$_2$ with NaOH is very straightforward. In this case, the flux is easily premelted (320°C) in a quartz crucible, and the GeO$_2$ added directly. The resulting hexagonal and tetragonal, white, solid melts were dissolved completely in 45 and 75 mL of 2.5N NaOH, respectively. The reaction

$$GeO_2 + 2NaOH \rightleftharpoons Na_2GeO_3 + H_2O \qquad (14)$$
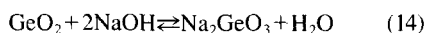
applies. Essentially complete solubilization of GeO$_2$ is obtained with these fluxes (Table III).

Fusion under reducing conditions with sodium hypophosphite also proceeds readily. The flux mixture ignites and, after burning, forms a melt that dissolves completely in heated 2.5M NaOH. Upon cooling, the entire solution forms a clear crystalline mass that dissolves completely in 6M HCl. The low recovery of Ge could be due to loss of the volatile monoxide during reductive fusion. Sodium formate also ignites during fusion. The resulting solidified melt does not dissolve completely upon heating with 2.5M NaOH. Additional treatment with 30% H$_2$O$_2$ also failed to solubilize the remaining residues, which are largely carbon deposits. Fusions with sodium oxalate were found to behave similarly, with the exception that the flux does not ignite upon heating. After prolonged heating of h-GeO$_2$ with this flux material in a Ni crucible, a gray product was formed that did not dissolve completely when treated with 2.5M NaOH. The relative amounts of GeO$_2$ solubilized by the various fusion procedures are reported in Table III. Moderate temperature fusion in quartz vessels may evidently be based on the reactions either with NaOH or with Na$_2$O$_2$ for conversion of chemically intractable t- or h-GeO$_2$ into the reactive form. These flux materials are readily available and inexpensive and effect quantitative solubilizations at moderate temperatures. Optimum flux/GeO$_2$ ratios, temperature, and time of fusion are easily assessed.

SUMMARY AND CONCLUSIONS

This report describes a variety of chemical procedures that have been examined for potential use in large, industrial-scale processing of GeO$_2$ raw materials that, under ordinary conditions, possess low chemical reactivity and poor solubilization properties. Stockpiles of chemically intractable GeO$_2$ raw materials such as those examined in this study may be available. These materials may be processed efficiently and economically by methods described in this work and converted into technologically desirable and increasingly expensive Ge compounds such as GeO$_4$. Solubilization and fusion procedures leading to formation of soluble (aqueous) Ge species have been described. These processes may be used to produce GeCl$_4$ by the conventional distillation method, employing concentrated HCl–Cl$_2$. Exothermic processes in the 600° to 700°C region were not detected in any of the other samples. This effect, we suspect, is due to residual water of hydration which is only completely removed from the oxide above 800°C, as possibly indicated by the weak endotherm in the 840° to 900°C region. The lower temperature endotherm could thus be explained by hydrothermal conversion of some hexagonal material to the tetragonal form, which is more stable by approximately 6 kcal/mol.[4]

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