

Hafnium Germanate from a Hydrous Hafnium Germanium Oxide Gel

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The gel chemistry of germanium is explored through the formation and composition of a hydrous metal oxide precursor gel used in the preparation of the HfGeO_4 and $\text{HfGeO}_4\text{:Ti}$ X-ray phosphors. The enhanced solubility of hexagonal GeO_2 in dilute ammoniacal solutions is exploited to give a convenient and high-yield precipitation. The precursor gel is shown by FT-IR to be a diphasic mixture of hydrous hafnia and an ammonium germanate gel. Thermal treatment drives the crystallization of a hafnium-rich, simple tetragonal $\text{Hf}_{1-x}\text{Ge}_x\text{O}_2$ structure at 893 °C, that upon further heating to 1200 °C yields scheelite HfGeO_4 .

Introduction

The oxide chemistry of germanium exhibits similarities to that of silicon, its group IVB neighbor. The ubiquitous 4-fold geometry of the silicates is expressed in the meta- and orthogermanates; however, the crystallization of tetragonal GeO_2 and other complex germanates in structures containing 6-fold coordination implies that germanium emulates tin chemistry. The gel chemistry of germanium also deviates from that of silicon. Distinct preparative and structural differences are apparent between germanium and silicon gels. Laubengayer and Brandt¹ ascribed the ease of silica gel formation relative to that of germania gels to the higher solubility of GeO_2 , which tends to encourage crystallization. Mukherjee has examined the $\text{SiO}_2\text{--GeO}_2$ gel and glass system,² as well as crystallization kinetics in the PbO--GeO_2 system,³ and the effects of Ge^{4+} coordination on the crystallization of a germanate gel.⁴ In this paper we describe the preparation of another germanium system, a hydrous hafnium germanium oxide gel, and contrast its high-temperature crystallization with that of the analogous silicate composition.

Zirconium germanate, ZrGeO_4 , was first prepared and identified as a member of the scheelite structural family by Bertaut and Durif.⁵ Lefèvre and Collongues, in their studies of the $(\text{Zr,Hf})\text{O}_2\text{--GeO}_2$ systems,^{6–8} described the preparation of HfGeO_4 and the structurally related Hf_3GeO_8 phase. Traditional solid state and precipitation methods have been applied in the synthesis of these germanates. Our interest in HfGeO_4 relates to its application as an X-ray phosphor for conventional radiography. The high density of the compound (8.5 g/cm³) provides exceptional X-ray absorption, particularly under the irradiation conditions used in mammography. Undoped HfGeO_4 produces an ultraviolet emission at ~350 nm under X-ray

excitation,⁹ while titanium-activated HfGeO_4 is an efficient X-ray phosphor with a broad-band emission centered at 425 nm.^{10,11}

Experimental Section

Materials. $\text{HfOCl}_2\cdot 8\text{H}_2\text{O}$ (Teledyne Wah Chang Albany, 0.026 mol % Zr, RGS) and GeO_2 (Eagle-Picher, hexagonal, or α form, 99.999%) were used as starting materials for the preparation of hydrous hafnium germanium oxide gel, hydrous hafnia, and ammonium germanate. Ammonium titanyl oxalate, $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2\cdot \text{H}_2\text{O}$ (Johnson Matthey, 99.998%), was used for the titanium-doped gels. NH_4OH (ACS reagent grade, Eastman Fine Chemicals, standardized at 14.45 M) was used as the precipitating agent. NH_4Cl (ACS reagent grade, Eastman Kodak Co.) was used in the coagulation of the ammonium germanate samples.

Hydrous Hafnium Germanium Oxide Gel. To a rapidly mixed 1.5 M solution of $\text{HfOCl}_2\cdot 8\text{H}_2\text{O}$ was added 1 molar equiv of solid hexagonal GeO_2 , followed by the dropwise addition of concentrated NH_4OH . An increase in turbidity was observed almost immediately, followed by a severe thickening at pH ~4. Base addition continued until the pH of the solution/gel mixture reached ~9. The collected gel was washed in water (~3 mL/g of gel) and dried at 95 °C. At this point, the gel was amorphous (by X-ray powder diffraction) and contained ~14 wt % combined water and ammonium ion. The yield was ~100 g of dried gel/L of solution.

Ammonium Germanate Solution and Gel by Evaporation. An aqueous germanium oxide solution was prepared by dissolving 12 g of GeO_2 in 200 mL of distilled H_2O with the slow addition of 12 mL of concentrated NH_4OH (final pH ~9). Evaporation of the solution at 40 °C yielded a colorless and transparent solid gel.

Ammonium Germanate Gel by Chloride Addition. An ammonium germanate gel was prepared by the slow addition of 12 mL of concentrated NH_4OH to 200 mL of a 0.3 M NH_4Cl solution in which 12 g of solid GeO_2 was vigorously stirred. The final pH was ~9.

Physical Methods. Samples were fired to temperatures of 250–1200 °C in air in a box furnace with a constant heating rate of 10 °C/min. Dwell time at each temperature was 5 min. Powder diffraction patterns were initially obtained with an Enraf Nonius FR552 Guinier camera with $\text{Cu K}\alpha_1$ radiation. The powder diffractometer scans presented in the figures were obtained on a Rigaku RU 300 powder diffractometer equipped with a Cu rotating anode at a scan rate of 2°

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(2 θ)/min and a step size of 0.02°. Lattice parameters were determined by the least-squares method with a modified version of the Novak and Colville¹² templates. Differential thermal (DTA) and thermogravimetric (TGA) analyses were performed in air with heating rates of 10 °C/min on a Harrop DT 736 and a Cahn TG-141, respectively. Infrared spectra between 4000 and 200 cm⁻¹ were acquired on a Perkin-Elmer 1600 FT-IR. Samples (1–4 mg) were ground with ~400 mg of CsI (Johnson Matthey, 99.999%) and pressed into pellets. A blank sample of CsI was used for a background spectrum, and each sample spectrum consisted of 64 scans. The pH of the reaction solutions was monitored with a Corning 240 meter equipped with a combination electrode. Teledyne Wah Chang Albany Analytical Services determined nitrogen as NH₄⁺ by the Kjeldahl method and germanium via direct-coupled plasma emission.

Precipitation of Hydrous Hafnium Germanium Oxide Gel

HfGeO₄ can be prepared from direct combination of the oxides using standard solid-state techniques. This approach is limited by (1) the high-temperature volatility of GeO₂, (2) the decomposition of the scheelite phase above 1300 °C, and (3) the refractory nature of HfO₂. Several firing/grinding steps are required for complete phase formation. The preparation would clearly benefit from the convenience and inherent homogeneity of a hydrous metal coprecipitation.

Earlier synthetic work^{6–8} briefly described a precipitation method in which separate solutions of “soluble” (i.e., hexagonal) GeO₂ and hafnium oxychloride are combined, followed by precipitation with ammonium hydroxide. The mechanism of the precipitation was not discussed. The moderate solubility of hexagonal GeO₂ in water (4.5 g/L at 20 °C, 11.9 g/L at 100 °C) limits the yield of this preparation to ~15 g of dried gel/L of solution at room temperature.

To improve the yield, we sought an approach that enhanced the solubility of GeO₂. Two studies^{13,14} determined that the solubility of hexagonal GeO₂ is significantly increased in dilute ammoniacal aqueous solutions (up to ~160 g/L in a 1.2 wt % NH₃ solution). Each report suggested the generation of a soluble ammonium germanate; however, a consensus on the stoichiometry of this phase was not reached. At higher NH₃ concentrations, the solubility of GeO₂ decreases rapidly, as an amorphous gel is formed from the aggregation of an ammonium germanate sol. Eventually, at pH >9, hydrolysis yields solid GeO₂. The solubility of hexagonal GeO₂ is further enhanced in the tetramethyl- and tetraethylammonium hydroxides.¹⁵

Exploitation of this enhanced solubility is fundamental to the high-yield preparation of the hafnium germanium hydrous precursor. A concentrated HfOCl₂·8H₂O solution is combined with a stoichiometric amount of solid GeO₂. The dropwise addition of concentrated NH₄OH gives a stoichiometric gel at pH ≥9 (see the Experimental Section). A 7-fold yield increase is easily achieved with this procedure.

The pH dependence of the precipitation of a 0.29 mol aliquot of the hafnium germanium (1:1 molar ratio, 1 mol % Ti) hydrous oxide gel with 14.45 M NH₄OH is shown in Figure 1. Included is the titration curve for hydrous hafnia (1 mol % Ti) obtained under the same conditions. The latter curve is very similar to that described for hydrous hafnia.¹⁶ The coincidence of these two curves suggests that the acid–base behavior in the hafnium germanium hydrous oxide precipitation is due to the precipita-

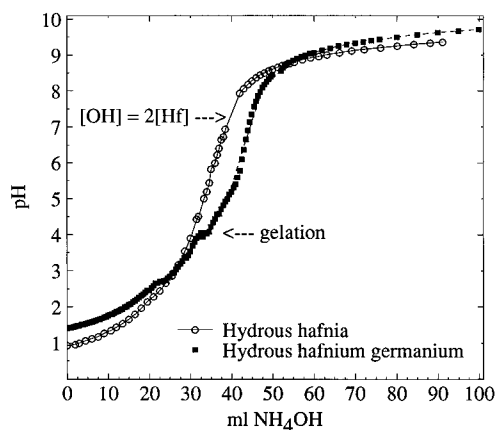


Figure 1. Titration for hydrous hafnia and hydrous hafnium germanium oxide.

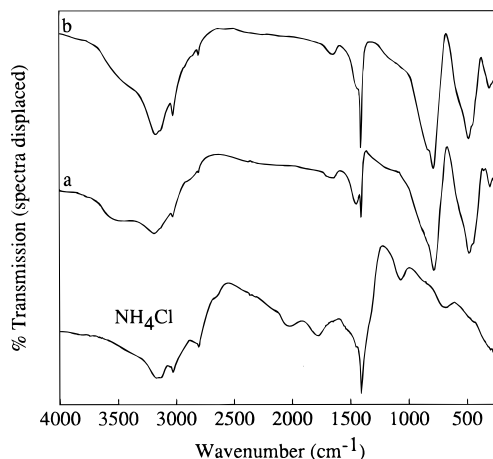


Figure 2. FT-IR spectra of ammonium germanate gel from (a) evaporation at 40 °C and (b) NH₄Cl addition.

tion of hydrous hafnia. The formation of the germanium component is best described as a complexation, not an acid–base reaction, and will be described in greater detail below.

Gel Composition and Formation

The composition of the precipitated hafnium germanium oxide gel is clarified by an examination of ammonium germanate gels. The infrared spectrum of a gel formed by evaporation of an ammonium germanate solution (see Experimental Section) is shown in Figure 2a. Vekhov et al.¹³ determined the composition of a similarly prepared gel as (NH₄)₂Ge₅O₁₁·7H₂O. This is in agreement with the findings of Everest and Salmon,¹⁷ who identified the pentagermanate anion as the stable species in aqueous solutions of pH 6–9.4.

Lyakh et al.¹⁴ suggest a composition of (NH₄)₃HGe₇O₁₆·nH₂O, identical to the crystalline phase described by Nowotny and Wittman.¹⁸ Elemental analysis of our gel gives a Ge⁴⁺:NH₄⁺ ratio of 2.72, which is greater than the theoretical values of 2.5 for (NH₄)₂Ge₅O₁₁·7H₂O and 2.3 for (NH₄)₃HGe₇O₁₆·nH₂O. This may be explained by the detection (by X-ray powder diffraction) of a small amount of hexagonal GeO₂ in the gel, possibly from the partial hydrolysis of the polygermanate anion.

Interestingly, the continued addition (pH >9) of NH₄OH to an aqueous ammonium germanate solution does not induce immediate gelation; only a slight turbidity is visible, and upon

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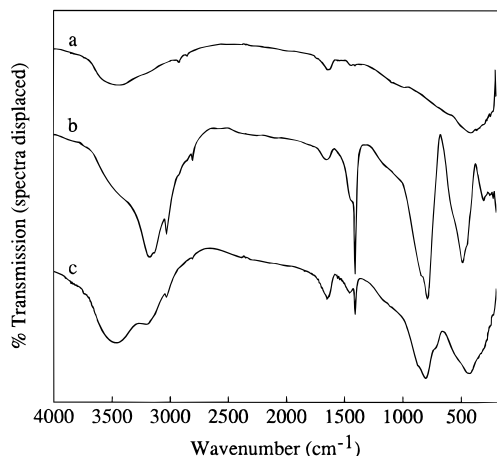


Figure 3. FT-IR spectra of (a) hydrous hafnia, (b) ammonium germanate, and (c) hydrous hafnium germanium oxide gel.

standing, a thin layer of white precipitate forms. In light of this result, the manner in which a 1:1 Hf:Ge stoichiometry is realized in the hydrous hafnium germanium oxide gel must be explained.

In contrast to the hydrous hafnium germanium oxide gel synthesis, chloride ion is absent in the above ammonium germanate preparation. To assess the influence of Cl^- , a 0.3 M NH_4Cl solution, which maintains the ionic concentration in the hafnium germanium oxide gel preparation, was used for the preparation of an ammonium germanate gel. A vivid coagulation was observed for $\text{pH} > 7$. The infrared spectrum of this gel, after a methanol wash and drying at 95°C , is shown in Figure 2b and is clearly comparable to that in Figure 2a.

For comparison, the infrared spectrum of NH_4Cl is shown in Figure 2. There are several similarities between the spectra, including sharp features at ~ 3170 , 3030 , 2807 , and 1408 cm^{-1} which correspond to normal or combination modes of the NH_4^+ group. The $\nu_2 + \nu_6$ and $\nu_4 + \nu_6$ combination modes observed¹⁹ in NH_4Cl at 2020 and 1772 cm^{-1} are either shifted or not active in the ammonium germanate samples. Additional differences are evident below 1200 cm^{-1} , where strong absorptions at 790 and 487 cm^{-1} are present in the ammonium germanate spectra. These features may be attributed to $\text{Ge}-\text{O}_n$ vibrations; however, assignment to either octahedral or tetrahedral geometry is complicated by the possible coexistence of both coordination spheres within the germanium polyanion component.²⁰

It is clear that the chloride ion is required for the immediate coagulation of the ammonium germanate component of the hafnium germanium oxide gel; however, Cl^- is not the only ion capable of promoting gelation. For example, the addition of a NH_4NO_3 solution to an ammonium germanate solution gives a gelation similar to that of NH_4Cl , albeit at a somewhat slower rate. Furthermore, the addition of a LiCl solution also yields a gel, but only after 24 h. This last result may indicate an interference by the Li^+ ion, rather than a lack of Cl^- effect. The anion-driven coagulation observed in the hafnium germanium oxide gel has not, to our knowledge, been reported for germanium oxide-based colloids.

In Figure 3a–c, the infrared spectra of the ammonium germanate gel (Figure 2b) is reproduced, along with spectra for a hydrous hafnium germanium oxide gel and a hydrous hafnia gel. The latter spectrum is in agreement with previous literature

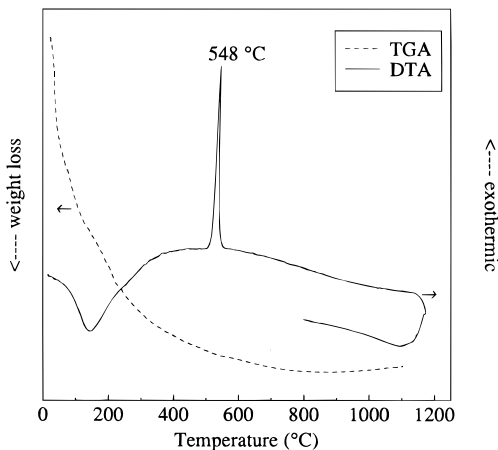


Figure 4. TGA (dashed) and DTA (solid) of hydrous hafnia.

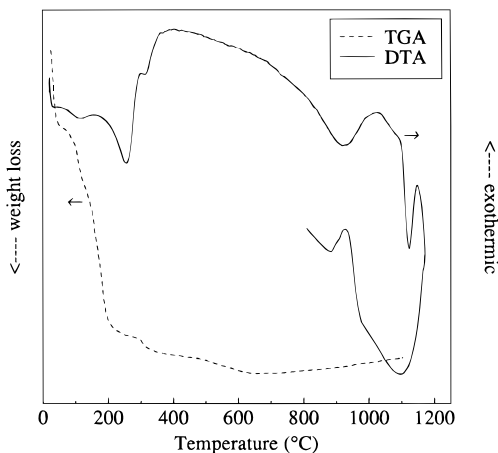


Figure 5. TGA (dashed) and DTA (solid) of ammonium germanate gel.

for $\text{Zr}(\text{OH})_4$.²¹ The hydrous hafnium germanium oxide gel appears to be a mixture of ammonium germanate and hydrous hafnia gels.

The results described above indicate that the precipitation occurs as follows: $\text{Hf}(\text{OH})_4$ is precipitated by the addition of NH_4OH in a similar fashion as represented in the titration of Figure 1. Concurrently, the solid GeO_2 is dissolved in the dilute ammoniacal solution. At $\text{pH} > 7$, after the complete dissolution of the GeO_2 powder, the ammonium germanate colloid begins to coagulate under the electrostatic influence of the Cl^- ion, and at $\text{pH} \sim 9$, the stoichiometric precipitation is complete. The process is described most accurately as a precipitation/coagulation.

Because excess ammonium ion is present in each of the ammonium germanate preparations described above, it is the presence of the chloride ion, a bystander ion at first glance, that promotes the gelation of the ammonium germanate component. This serendipity yields a stoichiometric hydrous hafnium germanium oxide gel.

Thermal Analysis—TGA and DTA

Figures 4 and 5 show TGA and DTA scans for hydrous hafnia and ammonium germanate, respectively. The thermal decomposition of hydrous hafnia is characterized by a gradual weight loss and a crystallization exotherm at 548°C . Ammonium germanate exhibits a richer thermal behavior, in which several

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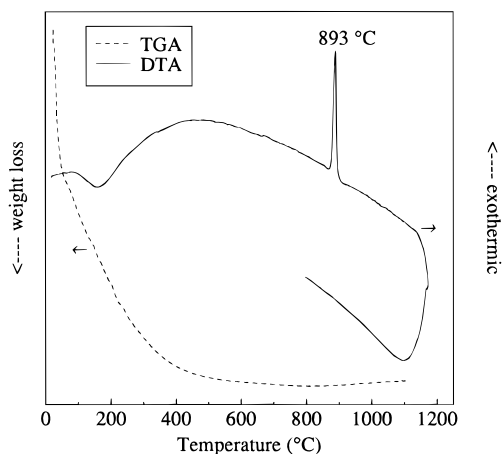


Figure 6. TGA (dashed) and DTA (solid) of hydrous hafnium germanium oxide gel.

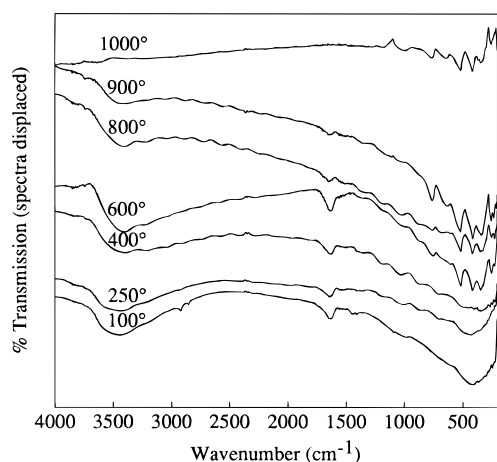


Figure 7. FT-IR spectra of hydrous hafnia vs temperature.

low-temperature weight losses correlate with DTA transitions associated with dehydration and ammonia evolution. At higher temperatures, a broad endotherm, possibly from a glass transition, is noticeable at 900 °C, followed by fusion of the sample at ~1120 °C.

Thermogravimetric analysis of a hydrous hafnium germanium oxide gel sample in air is shown in Figure 6. A gradual weight loss is visible up to ~400 °C, with no distinguishing features. A total weight loss of 13.9% is observed. The DTA exhibits a broad dehydration endotherm peaking at ~180 °C and a sharp crystallization exotherm at 893 °C.

Thermal Analysis—FT-IR and XRD

The FT-IR spectra of hydrous hafnia samples fired at different temperatures are shown in Figure 7. Minimal change is realized up to 600 °C. Below this temperature, the broad features of the spectra are similar with those observed for $Zr(OH)_4$ by Cabannes-Ott.²¹ The X-ray powder diffraction pattern indicates only the presence of an amorphous phase. At 600 °C, the spectrum shows a resolution of several peaks in the 300–700 cm^{-1} region, with a concurrent appearance of the broadened X-ray powder pattern of monoclinic hafnia. These features are consistent with the sharp crystallization exotherm observed in the DTA. At 1000 °C, the diffraction lines grow sharper and increase in intensity, and the FT-IR absorptions become more defined. At 1100 °C, the FT-IR spectrum is essentially the same as detailed in the literature.²²

The FT-IR spectra of fired ammonium germanate samples are compiled in Figure 8. Between 250 and 400 °C, the FT-IR

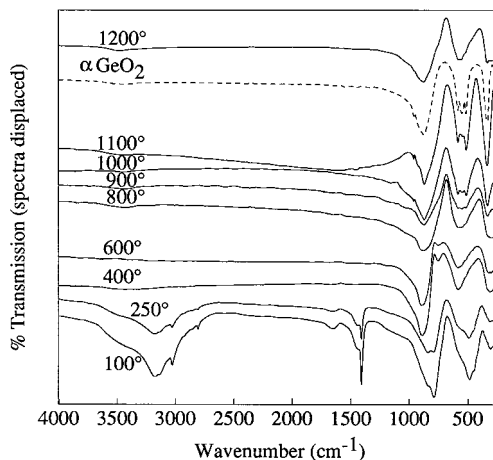


Figure 8. FT-IR spectra of ammonium germanate vs temperature.

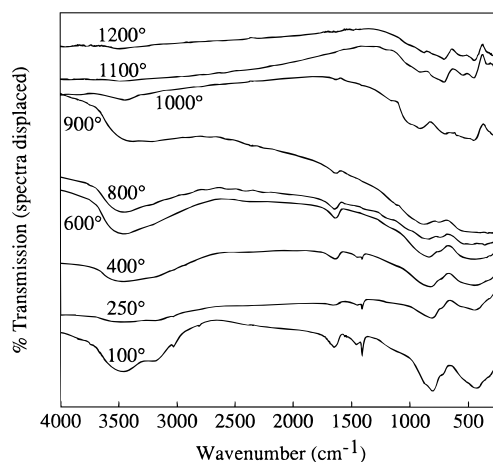


Figure 9. FT-IR spectra of hydrous hafnium germanium oxide gel vs temperature.

indicates that the bulk of the water and ammonium ion has been eliminated from the ammonium germanate sample. These effects are mirrored over the same temperature range in the TGA, where a major two-step weight loss is observed, and in the DTA, where a large two-stage endothermic effect is seen. The FT-IR spectrum at 400 °C shows broad features that correspond to the spectral features of hexagonal GeO_2 (spectrum included in Figure 8). This suggests a poorly crystalline hexagonal GeO_2 phase, which is consistent with the X-ray powder diffraction that shows only the broad major lines for hexagonal GeO_2 . As firing temperature increases, the FT-IR spectra reflect an evolution of fine structure identical with that of hexagonal GeO_2 . At 1000 °C, sharp diffraction peaks for hexagonal GeO_2 are observed, and the FT-IR spectrum is similarly indicative of the hexagonal phase. The 1200 °C sample, which had melted, shows a FT-IR spectrum and X-ray powder pattern similar to those for samples annealed at less than 900 °C. Upon melting and subsequent cooling, vitreous or poorly crystalline GeO_2 is commonly observed.²³

In Figure 9, the FT-IR spectra of fired hydrous hafnium germanium oxide gel samples are shown. The presence of ammonium ion is still indicated in the 400 °C sample, in contrast to the 400 °C ammonium germanate sample. The FT-IR spectra show a gradual broadening of features as the firing temperature is increased from 400 to 900 °C. The 800 cm^{-1} feature common

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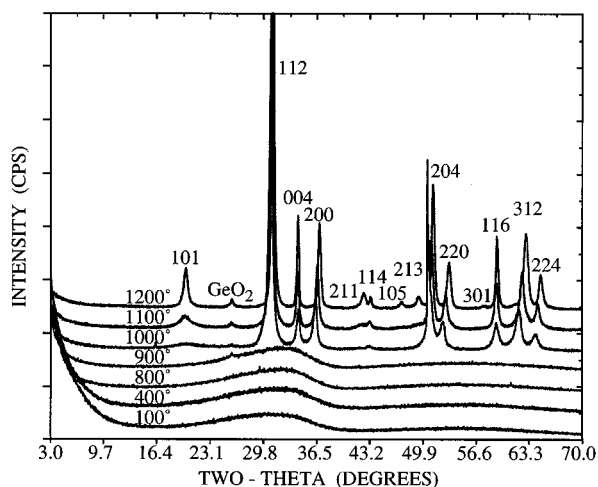


Figure 10. Powder diffraction patterns of hydrous hafnium germanium oxide gel vs temperature.

to ammonium germanate and hexagonal GeO_2 is retained in the hydrous hafnium germanium sample up to the crystallization temperature, as is the broad 500 cm^{-1} band associated with hydrous hafnia. Water is gradually eliminated from the material as evidenced by the reduction of the $-\text{OH}$ stretch centered at $\sim 3500\text{ cm}^{-1}$. Above the crystallization temperature, a fine structure gradually appears and finally yields a spectrum identical to that of previous vibrational studies of HfGeO_4 .²⁴

There is no evidence for crystallization in the X-ray powder diffraction patterns (Figure 10) of the gel samples heated at $<900^\circ\text{C}$; only a broad feature associated with an amorphous phase is apparent. At 900°C , a very weak line matching the strongest hexagonal GeO_2 diffraction peak is observed upon the background diffraction from the amorphous phase. Crystallization of the hafnium germanium oxide gel either has not yet yielded crystallites of sufficient size or has been compromised by the short dwell time.²⁵

At 1000°C , the X-ray pattern shows a broad simple tetragonal HfO_2 pattern similar to that described by Lefèvre.⁸ In the 1100°C sample, the peak positions in the simple tetragonal pattern shift in a manner consistent with a reduction in the a axis and an increase in c axis and an overall decrease in unit cell volume. For samples fired below 1200°C , Lefèvre⁸ described a $\text{Hf}_{1-x}\text{Ge}_x\text{O}_2$ solid solution in which increasing GeO_2 content mirrored the identical progression in lattice parameters. Finally, at 1200°C , the more complicated tetragonal scheelite pattern is apparent (see the indicated 101, 211, 105, 213 lines) with lattice parameters $a = 4.86\text{ \AA}$ and $c = 10.48\text{ \AA}$. Extended heating at 1200°C eventually yields a scheelite pattern with the lattice parameters $a = 4.854(1)\text{ \AA}$ and $c = 10.495(1)\text{ \AA}$. These cell dimensions are very similar to the literature values of $4.862(1)\text{ \AA}$ and $c = 10.497(1)\text{ \AA}$.²⁶

In Figure 10, a small amount of hexagonal GeO_2 is apparent in the powder patterns of those samples fired at above 900°C . Our initial X-ray examination, performed immediately after the preparation of the samples, showed no evidence of crystalline GeO_2 in these samples. Comparison of the two diffraction data sets showed no change in the diffraction line positions of the crystallized tetragonal phases. The crystallization, over the course of several months, of an amorphous germania component

is indicated. The presence of the amorphous phase is consistent with the Hf-rich $\text{Hf}_{1-x}\text{Ge}_x\text{O}_2$ phase that initially crystallizes.

Discussion

The crystallization appears to proceed with the nucleation of a hafnium-rich tetragonal $\text{Hf}_{1-x}\text{Ge}_x\text{O}_2$ phase and a small amount of crystalline and amorphous GeO_2 . As the firing temperature is raised, the germania component is incorporated into the $\text{Hf}_{1-x}\text{Ge}_x\text{O}_2$ phase with a decrease in cell volume. At higher temperatures, the Hf^{4+} and Ge^{4+} concentrations begin to equalize and the cations order into the scheelite lattice. Upon additional heating, the remaining GeO_2 is consumed and stoichiometric HfGeO_4 is formed. Note, the gradual ordering of the cations may also contribute to observed lattice parameter changes.

The direct crystallization of a hafnium germanium oxide phase from a diphasic amorphous oxide gel is unexpected in light of the thermal behavior of similar systems. For example, ZrSiO_4 (zircon), has been extensively studied, largely because of its application as a pigment host. Similar synthetic problems are apparent; a refractory oxide (ZrO_2 , HfO_2) is combined with an acidic oxide (SiO_2 , GeO_2). Unlike that of HfGeO_4 and ZrGeO_4 , the preparation of ZrSiO_4 is not restricted by the melting point of SiO_2 ($>1700^\circ\text{C}$) or by the decomposition temperature of the phase ($>1540^\circ\text{C}$).

Considerable effort has been focused on the preparation of high-purity ZrSiO_4 through the use of mineralizers,²⁷ processing of sol-gel precursors,²⁸ or the nanoheterogeneous seeding of the sol-gels.²⁹ The reactions usually proceed via the crystallization of a zirconia polymorph that subsequently combines, at high temperature, with a portion of the silica component. In the case of nanoheterogeneous sol-gel processing, the introduction of fine-particle zircon catalyzes the epitaxial growth of the phase.

In these examples there is no clear indicator, such as an exotherm in the DTA, of a sharp crystallization for the zircon phase similar to that observed for the hydrous hafnium germanium oxide gel. An explanation for this difference in crystallization may lie in the degree of $\text{Ge}-\text{O}-\text{Hf}$ connectivity within the gel structure at the intermediate annealing temperatures ($T > 400^\circ\text{C}$). Mori et al.²⁸ observed that the ZrSiO_4 yield increased with the amount of $\text{Zr}-\text{O}-\text{Si}$ linkages in dried gels as observed by infrared spectroscopy. The penchant of Ge^{4+} for octahedral coordination, as well as tetrahedral geometry, may enhance the degree of $\text{Hf}-\text{O}-\text{Ge}$ bonding within the gel structure. Unfortunately, distinct infrared bands associated with $\text{Hf}-\text{O}-\text{Ge}$ modes are likely to be obscured in the complex GeO_n portion of the hafnium germanium oxide gel spectra (Figure 9; $T > 400^\circ\text{C}$), and so a verification of the extent of $\text{Hf}-\text{O}-\text{Ge}$ linkage is not possible.

Conclusion

The exploitation of the enhanced solubility of hexagonal GeO_2 in dilute ammoniacal solutions leads to a high-yield preparation of a precipitated hydrous precursor for HfGeO_4 . The as-precipitated hydrous gel is a mixture of hydrous hafnia and an ammonium germanate gel. The mixture exhibits thermal behavior which is distinct from that of the respective compo-

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nents. This indicates an evolution to a homogeneous hydrous oxide gel. This progression is culminated with the crystallization of a $\text{Hf}_{1-x}\text{Ge}_x\text{O}_2$ phase that upon further heating yields stoichiometric HfGeO_4 .

The ammonium germanate solution route has also been used for the preparation of ZrGeO_4 and CeGeO_4 ¹⁵ and should provide a convenient pathway for the preparation of other germanates. As an example, Yukhin et al.³⁰ recently described the synthesis of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ from the reaction of bismuth oxohydroxonitrate with an ammonium germanate solution, followed by thermal

processing. The authors contrasted the convenience and high phase purity unique to this route with several traditional preparations of the orthogermanate.

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