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New Fluorination Reactions of Ammonium Bifluoride

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This paper describes a novel route for the production of low-oxygen-containing fluorozirconate glasses. The process involves the use of a hitherto unknown solid-state chemical reaction between ammonium bifluoride and specific anhydrous and hydrated metal fluoride salts. The products are defined as ammonium fluoride–metal fluoride complexes. The kinetics of their formation and subsequent dissociation were followed by thermogravimetric analysis. It was observed that these complexes decompose with the evolution of HF above temperatures at which ammonium bifluoride decomposes and where its supply may be exhausted. These materials have been used to melt fluorozirconate glasses. The oxygen contents of these glasses have been dramatically reduced to approximately 10 ppm. The glass stability, as defined by the lack of devitrification on reheating, also appears to increase with a lowering of the oxygen content. This implies that the mechanism of nucleation and growth is predominantly heterogeneous and not homogeneous nucleation. Furthermore, the production of long lengths of crystal-free fluoride fibers for transcontinental optical communication systems appears to be a realistic goal, especially if the heterogeneities can be eliminated. [Key words: glass, fluorides, processing, zirconate, ammonia.]

I. Introduction

The chance discovery of a fluorozirconate glass in France in 1974[1] has generated a great deal of interest over the years.[2-4] This has been brought about primarily by the ultralow attenuation of 10^{-2} to 10^{-3} dB/km theoretically predicted in the mid-infrared,[5] compared with the 0.15 dB/km realized for doped silica fibers at 1.55 μm. This has great practical implications for long-distance telecommunication systems which currently use doped silica fibers. Typically, these systems require repeaters every 30 km or so to reconstruct and amplify the signal. If fluorozirconate glass fibers achieve their theoretical loss, the repeater spacing will be dramatically increased, thereby reducing potential failure, installation and maintenance costs, and at the same time improving the quality of the signal.

Unfortunately, the present losses fall far short of the predicted 10^{-2} to 10^{-3} dB/km. In fact, the lowest losses reported to date are approximately 1 dB/km,[6] and these were measured on short lengths of fibers. The high losses have been attributed mainly to absorption due to transition metal ions, rare earths, and hydroxyl ions and also scattering losses due to impurity particles such as Pt, bubbles, fluoride and oxide crystals.[7-9] Although great improvements have been made in the purity of the starting materials, the powdered fluorides, along with the melts, are sensitive to moisture. Therefore, melting is usually performed under inert and dry conditions. It is common practice to add ammonium bifluoride, a known fluorinating agent, to fluorinate any oxide impurities at high temperatures, typically greater than 150°C. Based on this reaction, some researchers[10] use ZrO_2 as a starting material, as it can be easily obtained in reasonably high purity. The fluorination of ZrO_2 by ammonium bifluoride is given as

$$\begin{aligned} &2ZrO_2 + 7NH_4FHF \\ &\qquad \xrightarrow{150^\circ C} 2(NH_4)_3ZrF_7 + NH_3\uparrow + 4H_2O\uparrow \\ &\qquad\qquad \Big\downarrow {\scriptstyle 400^\circ C} \\ &\qquad\quad 2ZrF_4 + 6NH_4F \end{aligned} \tag{1}$$

However, whether one starts with 100% ZrO_2 or trace impurities of this or any other oxides, an unfortunate consequence of this reaction is that the ammonium bifluoride has a high dissociation rate above 150°C and so its supply may be exhausted before fluorination is complete. Secondly, the reaction of water (produced during fluorination) with anhydrous starting materials becomes more favorable at higher temperatures. The combination of these two factors will inevitably result in the formation of oxide scattering centers, especially if their solubility is low in fluoride glasses and melts. Therefore, under these conditions it is quite obvious that ammonium bifluoride will have limited success at removing the oxide particles. Hence, it is essential that the starting materials be completely dry and oxide-free and that perhaps reactive atmosphere processing (RAP) be used during melting. While RAP has the advantage of driving out the oxides, a disadvantage is that the extreme reactivity of most RAP reagents at high temperatures leads to attack of the crucible material, furnace liners, etc.

However, an alternative route is to use chemically modified starting materials such that they are an in situ source of fluorine at higher temperatures, especially beyond the fluorination range of ammonium bifluoride. The present paper describes the new reactions between ammonium bifluoride and some of the hydrated starting materials at room temperature which lead to the formation of chemically modified starting materials. The hydrated starting materials were used, as they are extremely pure with respect to transition metal and rare-earth ion impurities. The reactions and subsequent decompositions of the modified chemicals have been investigated using thermogravimetric analysis (TGA) from which activation energies for the reactions have been obtained. The possible reaction mechanisms are discussed. Also, the effect of the new reactions on the oxygen content in the fluorozirconate glasses has been investigated.

II. Experimental Procedure

Table I lists the high-purity compounds used in this study, along with their respective sources. Typically, the components were weighed out separately and then mixed together in the appropriate quantities such that the total mass was ap-

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Table I. Components and Their Sources

Component	Source
$ZrF_4 \cdot H_2O$	Teledyne, Albany, OR
$HfF_4 \cdot H_2O$	Teledyne
$AlF_3 \cdot H_2O$	NRL
ZrF_4 (doubly sublimed)	Cerac, Milwaukee, WI
AlF_3	BDH Chemicals
LaF_3	BDH Chemicals
BaF_2	BDH Chemicals
NaF	NRL
NH_4FHF	Fisher Scientific, Pittsburgh, PA BDH Chemicals
NH_4F	Allied Chemical, Chicago, IL

proximately 40 mg. The mixtures were subsequently placed in a platinum pan in a thermogravimetric analyzer.[‡] The TGA operated under flowing dry argon (120 cm^3/min) which was gettered prior to entering the TGA chamber. The heating rate was kept constant at 10°C/min, and the temperature inside the TGA chamber by the sample was calibrated against the melting point of indium. Depending on the experiment, the components were either heated isothermally at some predetermined temperature or heated to 900°C at 10°C/min with or without a prior isothermal treatment. The reaction products were analyzed using X-ray diffraction.[§]

The glasses were prepared with compositions approximating the nominal ZBLAN composition of 53 mol% ZrF_4, 20 mol% BaF_2, 4 mol% LaF_3, 3 mol% AlF_3, and 20 mol% NaF. Also, glasses were prepared by partial substitution of $ZrF_4 \cdot H_2O$ with $HfF_4 \cdot H_2O$. The glass compositions were weighed out in the appropriate quantities and subsequently melted in platinum crucibles and under dry argon. Several grams of ammonium bifluoride were added to facilitate fluorination. The melts were subsequently quenched and annealed and the glasses sent out for oxygen analysis.[¶] This technique consists of fusing the glass in a graphite crucible and measuring the evolved CO_2 using infrared spectroscopy. The detection limit of this technique is 10 ppm.

III. Results and Discussion

(1) $ZrF_4 \cdot H_2O$

Figure 1 shows the decomposition of $ZrF_4 \cdot H_2O$ as determined by thermogravimetric analysis. The $ZrF_4 \cdot H_2O$ decomposes at 225°C with the evolution of HF and H_2O, represented by peaks 1 and 2, respectively.[11,12] The product, ZrF_4, subsequently sublimes at 570°C (peak 3). However, the evolution of HF indicates that the $ZrF_4 \cdot H_2O$ dissociates to produce not only anhydrous ZrF_4 but also an oxide such as ZrO_2 or an oxyfluoride of zirconium.

$$ZrF_4 \cdot H_2O \rightarrow ZrF_4 + H_2O + HF + ZrO_xF_y \qquad (2)$$

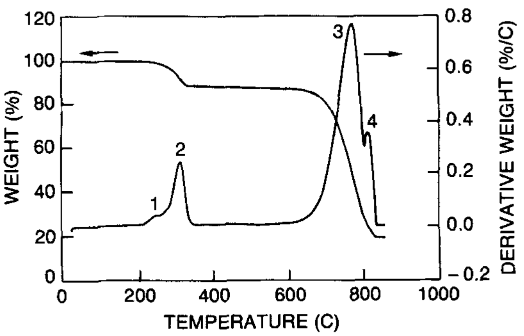


Fig. 1. TGA scan for the thermal decomposition of $ZrF_4 \cdot H_2O$.

Formation of an oxyfluoride is supported by the shoulder (peak 4) on the high-temperature side of peak 3. The shoulder presumably relates to the decomposition of a zirconium oxyfluoride compound (or compounds) of unknown stoichiometry into a less complex oxyfluoride/oxide. Unfortunately, the presence of this phase(s) cannot be substantiated by X-ray diffraction analysis because of the small quantity of this phase, typically less than 2 wt%. It should also be pointed out that the proposed oxyfluoride could also, in part, be the product of the "back-reaction" between the evolved H_2O and the anhydrous fluoride. Based on simple energetic considerations, this reaction is expected to be more favorable at higher temperatures. However, the reaction could be minimized by using a higher flow rate of argon, which would effectively reduce the residence time of the H_2O. Unfortunately, the flow rate used in these experiments was the maximum tolerable flow rate; a higher rate resulted in a disturbance and subsequent loss of the powdered sample material from the platinum pan in the TGA.

An unfortunate consequence of the dissociation of $ZrF_4 \cdot H_2O$ is the incorporation of zirconium oxyfluoride or oxide particles into a fluorozirconate glass or the fiber subsequently made from these starting materials. If these particles are not fluorinated, they will undoubtedly give rise to scattering centers and/or act as potential nuclei for subsequent crystal growth. Therefore, it is imperative to eliminate such species prior to melting by using either alternative starting materials or chemically modified starting materials. The latter approach has been employed in the present work. This has been achieved by reacting $ZrF_4 \cdot H_2O$ with ammonium bifluoride and is described in detail below.

The addition of ammonium bifluoride to $ZrF_4 \cdot H_2O$ at room temperature results in the evolution of heat and also HF as evidenced by moist blue litmus paper turning red.[13] X-ray diffraction analysis of the products revealed the presence of ammonium heptafluorozirconate, $(NH_4)_3ZrF_7$. Based on these observations, the reaction can be represented by the following equation:

$$ZrF_4 \cdot H_2O(s) + 3NH_4FHF(s) \rightarrow (NH_4)_3ZrF_7(s) + 3HF(g) + H_2O(g) \qquad (3)$$

As the reaction involves a weight change, it is possible to use thermogravimetric analysis to follow the reaction. Figure 2 shows the change in weight with time of a mixture of 1 mol of $ZrF_4 \cdot H_2O$ and 3 mol of NH_4FHF held isothermally at various temperatures. The rate of the reaction, which is represented by the slope of the curve, is initially high but decreases with time. The 30°C mixture was held isothermally for 3.5 d, whereas the other mixtures were held for approximately 18 h. For comparison, the decomposition of ammonium bifluoride is shown over a similar temperature range in Fig. 3.

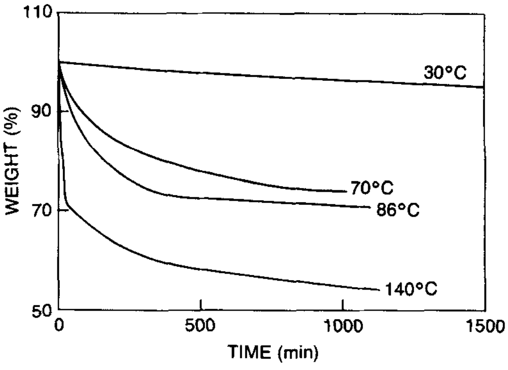


Fig. 2. Change in weight of a mixture of 1 mol of $ZrF_4 \cdot H_2O$ and 3 mol of NH_4FHF as a function of time at 30°, 70°, 86°, and 140°C.

[‡] Model 951, Du Pont Instruments, Wilmington, DE.
[§] McCrone Associates, Westmont, IL.
[¶] LECO Corp., St. Joseph, MI.

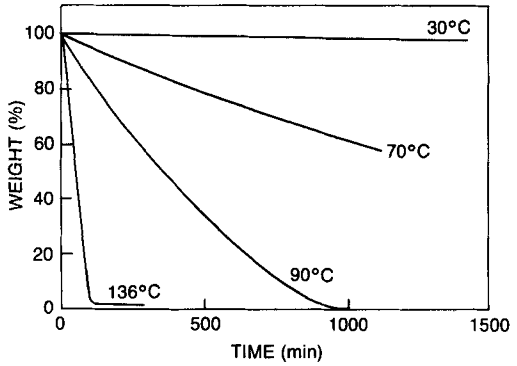


Fig. 3. Change in weight of ammonium bifluoride as a function of time at 30°, 70°, 90°, and 136°C.

After the isothermal treatments, the mixtures were heated to 900°C at a rate of 10°C/min. Figure 4 shows a plot of the change in weight as a function of temperature. The y-axis represents the derivative of the weight change with respect to temperature and allows for easier identification of the decomposition of any compounds. The weight losses due to such decompositions are easily identified by peaks in the derivative curve.

If the components are mixed and immediately heated without a prior isothermal treatment, the upper curve is obtained in which 7 peaks are clearly identifiable and have been labeled accordingly. By a careful review of the literature,[14-17] peaks 1 to 5 can be ascribed to the formation of $(NH_4)_3ZrF_7$ and its subsequent decomposition. It is proposed that the decomposition of $(NH_4)_3ZrF_7$ occurs as follows:

$$\begin{array}{l} ZrF_4 \cdot H_2O + 3NH_4FHF \\ \qquad \xrightarrow{1} (NH_4)_3ZrF_7 + 3HF + H_2O \\ \qquad\qquad \downarrow 2 \\ \qquad (NH_4)_2ZrF_6 + NH_4F \\ \qquad\qquad \downarrow 3 \\ \qquad NH_4ZrF_5 + NH_4F \\ \qquad\qquad \downarrow 4 \\ \qquad ZrF_4(\text{solid}) + NH_4F \\ \qquad\qquad \downarrow 5 \\ \qquad ZrF_4(\text{sublimed}) \end{array} \tag{4}$$

Furthermore, peaks 1 to 5 can be ascribed to reactions 1 to 5, respectively. For example, peak 1 represents the weight change due to the formation of $(NH_4)_3ZrF_7$ and the subsequent liberation of HF and H_2O. It should be pointed out that the present authors have investigated the decomposition of NH_4F using TGA and found it to be unstable above approximately 125°C. Ammonium fluoride sublimes at this temperature to produce HF and NH_3 gases. Therefore, it is concluded that NH_4F will be unstable at temperatures greater than 125°C and so reactions 2, 3, and 4 can be easily monitored using TGA. Also, as reactions 2, 3, and 4 involve the liberation of an equivalent quantity of NH_4F, it is quite understandable that the areas under peaks 2, 3, and 4 are also approximately equivalent.

However, there are two extra peaks which are not related to the decomposition of $(NH_4)_3ZrF_7$. For instance, peak 6 is attributed to the decomposition of unreacted ammonium bifluoride. This was confirmed by comparing peak 6 to the peak obtained for the decomposition of pure ammonium bifluoride. In addition, excess ammonium bifluoride was also added to $ZrF_4 \cdot H_2O$ and heated. The intensity of peak 6 subsequently increased, indicative of more unreacted ammonium bifluoride.

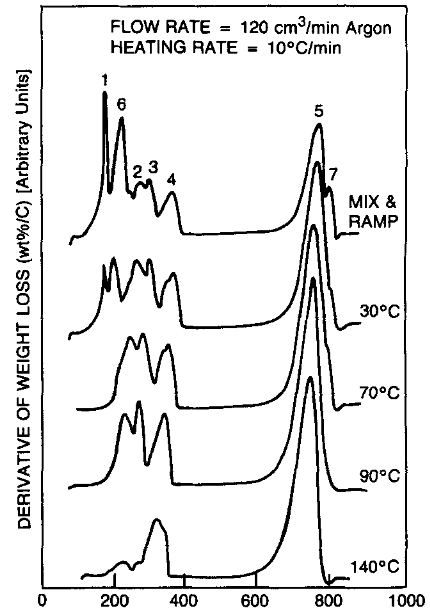


Fig. 4. Change in the derivative weight loss on heating the products of the isothermal reactions shown in Fig. 2. The upper curve was obtained by immediately heating a fresh mixture of $ZrF_4 \cdot H_2O$ and $3NH_4FHF$.

Peak 7 is considered to arise from the decomposition of a zirconium oxyfluoride(s) compound of unknown stoichiometry into a less complex oxyfluoride compound or ZrO_2. The presence of the oxyfluoride compound presumably implies incomplete fluorination of the $ZrF_4 \cdot H_2O$. This can be attributed to two factors. Firstly, as the decomposition rate of ammonium bifluoride is high above 150°C it is conceivable that some $ZrF_4 \cdot H_2O$ can remain unfluorinated since the efficiency (i.e., kinetics) of the fluorination reaction is unknown. Secondly, one cannot completely rule out the possibility of a reaction between the liberated H_2O and anhydrous ZrF_4.

It is immediately obvious that peak 1 disappears with increasing isothermal treatment temperature. The implications are that reaction 1 is completely over. For example, after heat-treating a mixture of 1 mol of $ZrF_4 \cdot H_2O$ and 3 mol of NH_4FHF for 17 h at 70°C, there is no trace of peak 1. In fact X-ray diffraction analysis reveals that the product is 100% $(NH_4)_3ZrF_7$ and therefore reaction 1 is complete. On the other hand, the dissociation of the products of the 140°C isothermal treatment (represented by the lower curve in Fig. 4) appears at first sight to be rather more complex. For instance, the intensity of peaks 2 and 3 seems to have decreased drastically. However, it is conceivable that as the dissociation rate of ammonium bifluoride is high at 140°C, then complete fluorination has not taken place. Instead, partial fluorination has resulted in the formation of mainly NH_4ZrF_5, although small quantities of $(NH_4)_3ZrF_7$ and $(NH_4)_2ZrF_6$ are also evident as well as $ZrF_4 \cdot H_2O$.

By careful examination of the curves it is possible to obtain the onset temperatures for the reactions 1 to 5 in Eq. (4). These data are tabulated in Table II. The present values compare favorably with those of Bragglia *et al.*[14] Although Bragglia *et al.* used a similar heating rate of 10 C/min, they used DSC rather than TGA. Despite the difference in the nature of the two experimental techniques, the values are in close agreement. However, the values expressed by Epov and Mikhailov[15] differ by more than 150°C. First of all, their values represent the temperatures corresponding to the midpoint of the peak on

Table II. Transformation Temperatures for the $ZrF_4 \cdot H_2O$ System

Transformations	Transformation temp (°C)			
$ZrF_4 \cdot H_2O + 3NH_4FHF \rightarrow (NH_4)_3ZrF_7$				30
$(NH_4)_3ZrF_7 \rightarrow (NH_4)_2ZrF_6$	140	315	120	149
$(NH_4)_2ZrF_6 \rightarrow NH_4ZrF_5$	195	365	125	204
$NH_4ZrF_5 \rightarrow ZrF_4$	275	435	200	269
ZrF_4(solid) → ZrF_4(sublimed)				570
$NH_4FHF \rightarrow NH_4FHF$(sublimed)				150
$ZrF_4 \cdot H_2O \rightarrow ZrF_4 + H_2O/HF + ZrO_xF_y$				220
References	14	15	16	This work

the derivative TGA plot and so cannot be used to define the onset of the appropriate dissociations. Secondly, there is no indication of sample size. This is an important parameter, as the midpoint of a peak on the derivative TGA plot will shift to higher temperatures with larger sample sizes. Therefore, their data suggest that they must have used larger sample sizes than in the present investigation. Furthermore, the values quoted by Gaudreau[17] were obtained by using a heating rate of 0.2°C/min. Although there are some similarities between his data and ours, there is still some discrepancy. Despite this, the underlying message from our particular experiments lies in the uniqueness of the solid-state room-temperature reaction between ammonium bifluoride and, in this case, zirconium fluoride.

(2) $HfF_4 \cdot H_2O$

The thermal decomposition of $HfF_4 \cdot H_2O$ is shown in Fig. 5. Hafnium fluoride monohydrate starts to decompose at 280°C, with the evolution of HF and H_2O represented by peaks 1 and 2, respectively. The decomposition is complete after 400°C under the heating conditions used. The evolution of HF is indicative of dissociation of the $HfF_4 \cdot H_2O$ into a hafnium oxyfluoride, akin to the decomposition of $ZrF_4 \cdot H_2O$. The decomposition of this oxyfluoride compound is represented by peak 4. Similar to the fluorozirconates, there is the possibility of incorporating potential scattering centers in fluorohafnate glasses if the $HfF_4 \cdot H_2O$ is incompletely fluorinated. However, on mixing 1 mol of $HfF_4 \cdot H_2O$ with 3 mol of NH_4FHF at room temperature, heat is generated, indicating that a reaction has occurred. Also, moist blue litmus paper turns red, suggesting that HF gas is liberated. The reaction has been followed in more detail by using TGA at different temperatures as shown in Fig. 6. The reaction proceeds rather slowly at room temperature (30°C) but the rate of the reaction increases with temperature. X-ray diffraction analysis of the products reveals, in analogy with the $ZrF_4 \cdot H_2O$ and NH_4FHF reaction (Eq. (4)), that the reaction between $HfF_4 \cdot H_2O$ and NH_4FHF occurs according to the first equation of the following sequence:

$$\begin{aligned}
&HfF_4 \cdot H_2O + 3NH_4FHF \\
&\qquad \xrightarrow{1} (NH_4)_3HfF_7 + 3HF + H_2O \\
&\qquad\qquad \downarrow 2 \\
&\qquad (NH_4)_2HfF_6 + NH_4F \\
&\qquad\qquad \downarrow 3 \\
&\qquad NH_4HfF_5 + NH_4F \\
&\qquad\qquad \downarrow 4 \\
&\qquad HfF_4(\text{solid}) + NH_4F \\
&\qquad\qquad \downarrow 5 \\
&\qquad HfF_4(\text{sublimed})
\end{aligned} \tag{5}$$

The products of the isothermal reactions were subsequently heated to 900°C at 10°C/min. The derivative of the weight loss as a function of temperature is shown versus temperature in Fig. 7. Also shown for comparison in the top curve is a mixture of 1 mol of $HfF_4 \cdot H_2O$ and 3 mol of NH_4FHF which was heated immediately after mixing. The peaks in the TGA plot are labeled according to the reaction scheme proposed. There are two extra peaks evident in the plot labeled 6 and 7. As before, these correspond to the dissociation of ammonium bifluoride and $HfF_4 \cdot H_2O$, respectively, based on a comparison between their dissociation curves and also by selectively adding excess ammonium bifluoride or hafnium fluoride monohydrate to the mixtures prior to heating. This implies that the reaction is not complete at room temperature, even after 3.5 d. However, peak 7 persists even after the 100°C isothermal treatment, suggesting that the $HfF_4 \cdot H_2O$ is not completely fluorinated. Incomplete mixing of hafnium fluoride monohydrate and ammonium bifluoride could possibly account for this observation.

Table III lists the temperatures of the various reactions and decompositions.

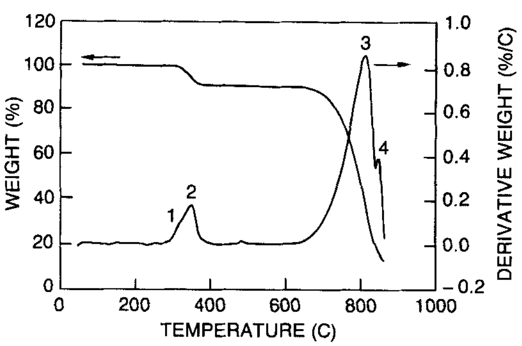


Fig. 5. TGA scan for the thermal decomposition of $HfF_4 \cdot H_2O$.

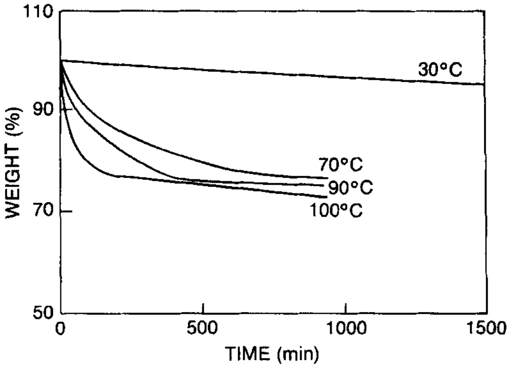


Fig. 6. Change in weight of a mixture of 1 mol of $HfF_4 \cdot H_2O$ and 3 mol of NH_4FHF as a function of time at 30°, 70°, 90°, and 100°C.

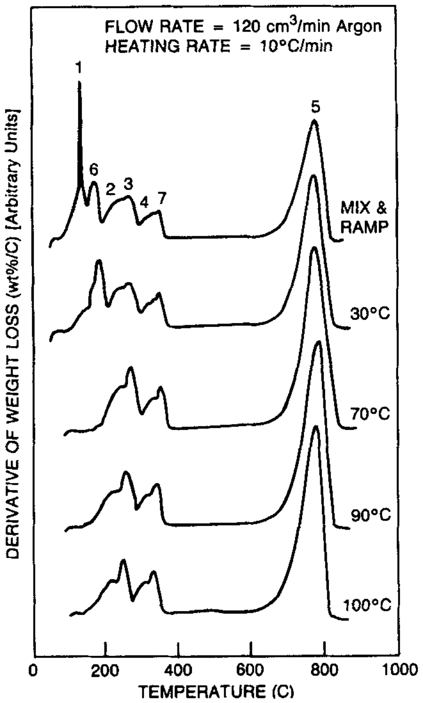


Fig. 7. Change in the derivative weight loss on heating the products of the isothermal reactions shown in Fig. 6. The top curve was obtained by immediately heating a fresh mixture of $HfF_4 \cdot H_2O$ and $3NH_4FHF$.

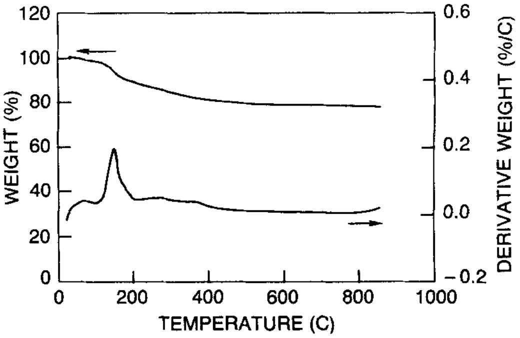


Fig. 8. TGA scan for the thermal decomposition of $AlF_3 \cdot H_2O$.

(3) $AlF_3 \cdot H_2O$

The dissociation of $AlF_3 \cdot H_2O$ results in a peak whose onset is at approximately 100°C (Fig. 8) due to the evolution of H_2O. The final yield is 79.5% of the original weight, whereas the theoretical yield of AlF_3 should be 82.4% of the original weight. This implies that the product is not pure anhydrous AlF_3. This difference can be attributed to the decomposition of aluminum hydroxide, $Al(OH)_3$, into boehmite, AlO(OH) which causes the peak centered at 267°C (onset 220°C). This was confirmed by observing the decomposition of a sample of pure $Al(OH)_3$. Boehmite is known to decompose into Al_2O_3 at 450°C. Therefore, the presence of this oxide phase, if it goes unfluorinated, will inevitably result in the presence of scattering centers.

However, the addition of 1 mol of $AlF_3 \cdot H_2O$ to 3 mol of NH_4FHF results in a reaction as evidenced by the liberation of HF and heat. The reactions were followed with TGA at different temperatures as shown in Fig. 9. Again, as for the systems already described, the reaction rate between the two components is initially high but decreases with time. X-ray diffraction analysis of the products reveals the presence of ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$, and ammonium tetrafluoroaluminate, NH_4AlF_4. Based on this it is possible to represent the reaction between $AlF_3 \cdot H_2O$ and NH_4FHF and the subsequent decomposition of the reaction products by the following equations:

$$\begin{array}{l} AlF_3 \cdot H_2O + 3NH_4FHF \\ \qquad \xrightarrow{1} (NH_4)_3AlF_6 + 3HF + H_2O \\ \qquad\qquad \downarrow 2 \\ \qquad NH_4AlF_4 + 2NH_4F \\ \qquad\qquad \downarrow 3 \\ \qquad AlF_3 + NH_4F \end{array} \tag{6}$$

Based on X-ray diffraction analysis, the above reaction scheme, and the weight loss (from Fig. 9), it is possible to estimate both the nature and the quantity of the products. These results are shown in Table IV. The last column in Table IV was obtained by recording the quantity of AlF_3 obtained after heating the products of the isothermal reaction. It was then possible to back-calculate and predict the possible quantity and nature of the starting materials. The agreement between the two sets of data is reasonably good. Any large discrepancies would indicate that the decomposition rate of ammonium bifluoride is high and so it is decomposing and not reacting. However, this was not the case (within 10%), and therefore the decomposition rate of ammonium bifluoride is low enough not to greatly affect the reaction.

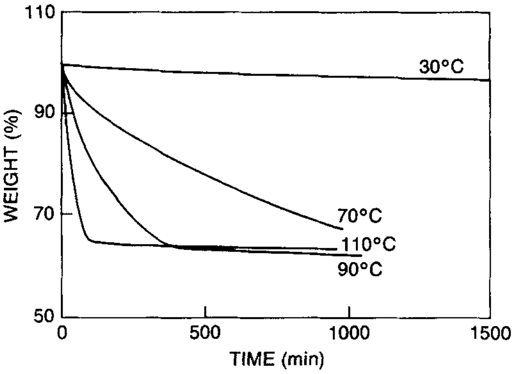


Fig. 9. Change in weight of a mixture of 1 mol of $AlF_3 \cdot H_2O$ and 3 mol of NH_4FHF as a function of time at 30°, 70°, 90°, and 110°C.

Table III. Transformation Temperatures of the $HfF_4 \cdot H_2O$ System

Transformations	Transformation temp (°C)
$HfF_4 \cdot H_2O + 3NH_4FHF \rightarrow (NH_4)_3HfF_7$	30
$(NH_4)_3HfF_7 \rightarrow (NH_4)_2HfF_6$	215
$(NH_4)_2HfF_6 \rightarrow NH_4HfF_5$	271
$NH_4HfF_5 \rightarrow HfF_4$(solid)	321
HfF_4(solid) $\rightarrow HfF_4$(sublimed)	621
$HfF_4 \cdot H_2O \rightarrow HfF_4 + H_2O/HF + HfO_xF_y$	280

Table IV. Estimated Products of the $AlF_3 \cdot H_2O$ and NH_4FHF Reaction

Isothermal treatment temp (°C)	Estimated products of isothermal reaction (mol%)	Predicted products based on AlF_3 yield (mol%)
30	90% [$AlF_3 \cdot H_2O + 3NH_4FHF$] 10% $(NH_4)_3AlF_6$	90% [$AlF_3 \cdot H_2O + 3NH_4FHF$] 10% $(NH_4)_3AlF_6$
70	87% $(NH_4)_2AlF_6$ 13% NH_4AlF_6	97% $(NH_4)_2AlF_6$ 3% NH_4AlF_6
90	65% $(NH_4)_3AlF_6$ 35% NH_4AlF_4	78% $(NH_4)_3AlF_6$ 22% NH_4AlF_4
110	71% $(NH_4)_3AlF_6$ 29% NH_4AlF_4	81% $(NH_4)_3AlF_6$ 19% NH_4AlF_4

Once the mixtures had been left to react isothermally for approximately 17 h, they were subsequently heat-treated up to 900°C at 10°C/min under flowing argon. Figure 10 shows the change in weight of the mixture as a function of temperature. Again, the derivative of the weight loss was used to show the weight changes more clearly. The top curve represents a mixture of 1 mol of $AlF_3 \cdot H_2O$ and 3 mol of NH_4FHF which was simply mixed and heated immediately. Peaks 1, 2, and 3 correspond to the three reactions 1, 2, and 3, respectively, shown in reaction scheme (6). There is an extra peak 4 centered at approximately 175°C which is due to the decomposition of unreacted ammonium bifluoride. This shows that the reaction between ammonium bifluoride and $AlF_3 \cdot H_2O$ does not go to completion if the mixture is heated immediately after mixing the two components together. The relative intensities of peaks 1 and 4 to peaks 2 and 3 decrease with time at a given temperature, indicating that the reaction between ammonium bifluoride and $AlF_3 \cdot H_2O$ proceeds with time. For example, the intensities of peaks 1 and 4 decrease relative to peaks 2 and 3 when the mixture is held isothermally for 3.5 d at 30°C. Also, the same peaks decrease with temperature, implying that the reaction between ammonium bifluoride and $AlF_3 \cdot H_2O$ is more favorable at higher temperatures.

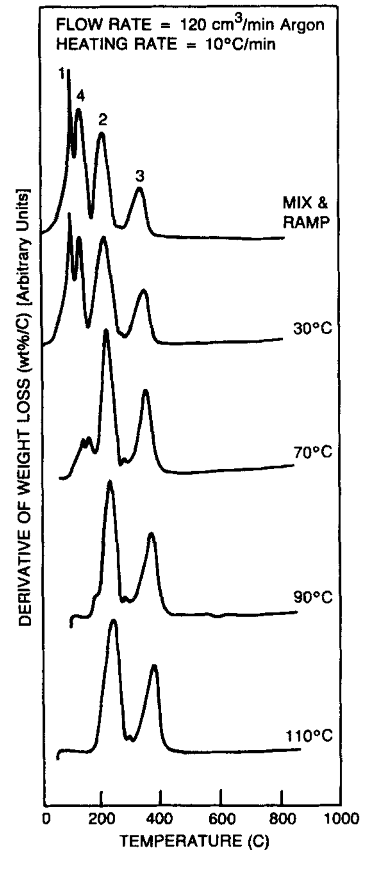


Fig. 10. Change in the derivative weight loss on heating the products of the isothermal reactions shown in Fig. 9. The upper curve was obtained by immediately heating a fresh mixture of $AlF_3 \cdot H_2O$ and $3NH_4FHF$.

The relative areas under peaks 2 and 3 are approximately 2:1. This agrees favorably with the predicted weight changes: namely, the decomposition of $(NH_4)_3AlF_6$ to NH_4AlF_4 (peak 2) produces 2 mol of NH_4F (which sublimes to NH_3 and HF), whereas the decomposition of NH_4AlF_4 to AlF_3 (peak 3) produces 1 mol of NH_4F. Also, in accordance with Table IV, the intensity of peak 3 increases relative to peak 2 because of the presence of residual NH_4AlF_4 in the mixtures which were isothermally reacted at 70°, 90°, and 110°C.

Table V shows the temperatures of the transformations.

(4) ZrF_4 and AlF_3

The anhydrous fluorides, ZrF_4 and AlF_3, react with ammonium bifluoride at room temperature. However, the reaction is not as vigorous as the reaction between the monohydrate salts and ammonium bifluoride. Based on X-ray diffraction analysis the reactions can be best represented by the following equations:

$$ZrF_4 + 3NH_4FHF \rightarrow (NH_4)_3ZrF_7 + 3HF \quad (7)$$

$$AlF_3 + 3NH_4FHF \rightarrow (NH_4)_3AlF_6 + 3HF \quad (8)$$

The subsequent decomposition of $(NH_4)_3ZrF_7$ and $(NH_4)_3AlF_6$ follows the same route as shown previously in this paper. The major difference between reactions (7) and (8) and their monohydrate salt counterparts is the exclusion of water as a product of the reaction with ammonium bifluoride.

(5) LaF_3, BaF_2, and NaF

Unlike the monohydrate salts described previously, and also ZrF_4 and AlF_3, the fluorides of lanthanum, barium, and sodium do not react with ammonium bifluoride under the conditions used in these experiments. Also, the authors have not found any ammonium fluoride complexes of these salts in the literature.

IV. Activation Energy

It is possible to represent the reaction between ammonium bifluoride and the fluoride salts by the following simple kinetic expression:

$$k = A \exp(-E/RT) \quad (9)$$

where k is the initial rate of weight loss, R is the universal gas constant, and E is the activation energy of the reaction. The value of k was taken as the initial slope of the weight loss versus time curves shown in Figs. 2, 3, 6, and 9. Therefore, k is

Table V. Transformation Temperatures for the $AlF_3 \cdot H_2O$ System

Transformations	Transformation temp (°C)
$AlF_3 \cdot H_2O + NH_4FHF \rightarrow (NH_4)_3AlF_6$	30
$(NH_4)_3AlF_6 \rightarrow NH_4AlF_4$	167
$NH_4AlF_4 \rightarrow AlF_3$	300

given by

$$\ln k = -E/RT + \ln A \tag{11}$$

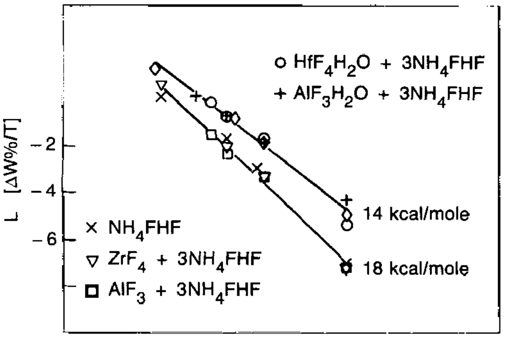
Figure 11 shows a plot of ln k against $1/T$ for all the reactions investigated except the salts which did not react with ammonium bifluoride. Two things are immediately obvious. Firstly, the data points lie on two separate lines. The reactions between ammonium bifluoride and the monohydrate salts lie predominantly on the upper line, while the thermal decomposition of ammonium bifluoride and the reactions between ammonium bifluoride and the anhydrous salts lie on the lower line. This implies that at any given temperature the rate of reaction between the monohydrate salts and ammonium bifluoride is higher than the reaction between the anhydrous salts and ammonium bifluoride. Secondly, the slopes of the two lines are approximately equal, indicating that the reaction mechanisms may be similar. The fact that the anhydrous salt reaction rates are comparable to the decomposition rate of ammonium bifluoride implies that the reaction could be a vapor phase reaction, depending primarily on the decomposed ammonium bifluoride. However, the reaction rate between the monohydrate salts and ammonium bifluoride is higher than the decomposition rate of ammonium bifluoride which implies that this is presumably a solid-state reaction. However, it should be pointed out that the role of adsorbed surface moisture is unknown. The driving force for the reactions may well be the liberation of HF and in the case of the monohydrate salts the liberation of HF and H_2O.

Glasses have been prepared by prior batching of the monohydrate salts with ammonium bifluoride at 70°C for approximately 18 h under flowing argon. The modified starting materials were then mixed together with the other anhydrous glass components and subsequently melted in the presence of ammonium bifluoride. It was important to heat the mixture at 500°C in order to ensure that complete dissociation of the ammonium fluoride–metal fluoride complexes had taken place prior to melting. The same experiments were performed but without prior modification of the starting materials (old glasses). Table VI shows the oxygen content of the new glasses along with typical values reported in the literature. The values reported by Takahashi *et al.*[18] were obtained on glasses prepared with anhydrous fluoride starting materials rather than the monohydrate materials used in the present study. However, the initial oxide content of their starting materials was not reported. It is quite apparent that the glasses prepared with the modified starting materials contain almost an order of magnitude less oxygen than similar glasses with no special pretreatment. This difference can be attributed to the presence of the ammonium fluoride complexes described in this paper which decompose at temperatures above that at which the ammonium bifluoride decomposes. The decomposition of these modified salts produces ammonium fluoride which dissociates into NH_3 and HF gases. Therefore, there is a fluorinating source (i.e., HF) available at temperatures above the decomposition of ammonium bifluoride where its supply may be exhausted.

Table VI. Oxygen Content of the Glasses*

Old glasses	
Takahashi[18]	
New glasses	10–50

*Analyzed by LECO Corp.



The stability of the glasses was ascertained by employing a method based on Drehman[19] and Hart *et al.*[20] The technique consisted of heating a 5-g chunk of glass at 290°C for 24 h in order to grow nuclei. The previous authors suggested that this temperature was low enough to inhibit crystal growth. The temperature was then raised to 340°C to grow crystals on the nuclei. The crystals were predominantly $2ZrF_4 \cdot BaF_2$ (2ZB). This temperature was chosen since the nucleation rate was negligible as confirmed by the absence of "appreciable" bulk crystallization on heating a fresh piece of glass at 340°C. Table VII shows the nucleation rates obtained, expressed in number of nuclei formed/cm^3/s^{-1}, for the present glasses compared with literature data. It is quite obvious that the present glasses are more stable, as they exhibit nucleation rates much lower than those of Drehman[19] and Hart *et al.*[20] In fact, many of the present glasses did not crystallize under the conditions used in this study. This result appears to contradict the observations of Drehman[19] and Hart *et al.*[20] who both found significantly higher nucleation rates. Despite the large differences in the nucleation rates shown in Table VII, Drehman[19] attributed the mechanism of nucleation to homogeneous nucleation and growth. This conclusion appears unwarranted as there is such a large difference between the different sets of nucleation data.

Hart *et al.*[20] proposed that heterogeneous nucleation was probably occurring as evidenced by the large variation in their nucleation data. For example, their measured nucleation rates varied over as much as 3 to 4 orders of magnitude for samples given the same nucleation treatment. They attributed this to contamination. Given this information and also the fact that many of the present glasses did not crystallize, it would appear that homogeneous nucleation is not the predominant nucleation mechanism under the conditions used. In fact, it would be more appropriate to replace the nucleation rate by the crystal density, defined as the number of crystals per cm^3. These data are shown in Table VII alongside the nucleation rates. It is quite apparent that the shear number of crystals obtained for the glasses in Refs. 19 and 20, compared to the present glasses, implies heterogeneous nucleation as the predominant mechanism of growth.

Furthermore, it is now possible to speculate on one source of heterogeneous nuclei. Although the oxygen content in Drehman's glasses was unknown, the crystal density data in

	Nucleation rate (nuclei/($cm^3 \cdot s$))	Crystal density (crystals/cm^3)
Old glasses and Ref. 20	10^1–10^{-3}	10^6–10^2
New glasses	$<10^{-4}$	10–0

conjunction with the oxygen data in Table VI suggest that oxygen can destabilize the glasses. It is postulated that oxygen, in the form of oxide/oxyfluoride impurities, may not be completely dissolved in the glasses and that, furthermore, these species can act as potential nuclei for subsequent crystal growth. Work is currently in progress in the authors' laboratory to explore this, and the results will be the subject of a future paper.

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