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Reaction of Zirconium Fluoride Monohydrate and Ammonium Bifluoride: Its Effect on Fluoride Glass Preparation and Quality

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The products obtained from the room-temperature reaction of ammonium bifluoride and zirconium fluoride monohydrate are ammonium heptafluorozirconate ($(NH_4)_3ZrF_7$), liquid water, and hydrogen fluoride. Ammonium bifluoride and zirconium fluoride monohydrate were reacted prior to glass batching, producing dry ammonium heptafluorozirconate which was used to prepare a high-quality ZBLAN fluoride glass. [Key words: glass, fluorides, ammonium, zirconium, processing.]

AMMONIUM BIFLUORIDE has long been used in the preparation of fluoride glasses to convert oxides such as zirconia into the corresponding fluorides.[1,2] We presently use ammonium bifluoride to fluorinate oxide impurities formed via thermal decomposition of zirconium fluoride monohydrate[3] in our ZBLAN glass-melting procedure. This processing technique generally produces high-quality fluoride glasses with respect to initial bulk crystallization. However, nucleation and crystallization studies[4] conducted on the glasses indicate decreased stability on remelting. The goal of this study is to determine the optimum conditions for preparing a stable, low-oxide ZBLAN glass using ammonium bifluoride as a fluorinating agent.

It is commonly assumed that ammonium bifluoride is relatively inert toward the ZBLAN fluoride glass batch until its decomposition into hydrogen fluoride and ammonium flouride occurs at high temperatures. Additionally, water formed as a result of the fluorination of oxides can be removed effectively by sweeping the batched chemicals with dry argon gas, leaving behind totally dry, fully fluorinated starting materials. We have observed that, shortly after addition of ammonium bifluoride to a 100-g ZBLAN fluoride glass batch, the resulting mixture begins to evolve heat, with the container eventually becoming hot to the touch. Liquid droplets often form on the walls of the batch container and the chemicals visibly increase in volume over a period of 1 to 2 d. This reactivity is not observed from mixtures of barium, lanthanum, or sodium fluorides with ammonium bifluoride, whereas mixtures of zirconium or hafnium fluoride monohydrate, aluminum fluoride monohydrate, and indium fluoride with ammonium bifluoride do display this behavior.

When zirconium fluoride monohydrate and ammonium bifluoride are mixed, the temperature of the resulting mixture increases within minutes. After 5 min the initially free-flowing powders form clumps, with continuous evolution of heat. A slurry results after approximately 5 h, indicating the presence of water, the most probable source of which is the decomposition of zirconium fluoride monohydrate, although water may be contributed by "wet" ammonium bifluoride. Moistened blue litmus paper turns red when exposed to the reaction atmosphere, indicating the presence of hydrogen fluoride gas. The gaseous products of the reaction conducted isothermally at 70°C were passed through a 1*M* sodium hydroxide solution to trap the evolved hydrogen fluoride as sodium fluoride. Back titration of this solution with 1*M* hydrochloric acid has shown that the reaction for *well-agitated* bulk samples, is complete after approximately 8 h at 70°C. We have detected the fluoride ion in the neutralized sodium hydroxide solution via a fluoride-ion selective electrode, verifying that hydrogen fluoride is indeed liberated from this reaction.

A stoichiometric mixture of high-purity zirconium fluoride monohydrate[‡] and ammonium bifluoride[§] was reacted for 8 d open to the atmosphere. The product, a dry agglomerate, was ground in a mortar and pestle and analyzed[¶] via powder X-ray diffraction (XRD). The composition of the product was determined to be 60% to 70% $(NH_4)_3ZrF_7$ and 30% to 40% $(NH_4)_2ZrF_6$, with no residual zirconium fluoride mono-

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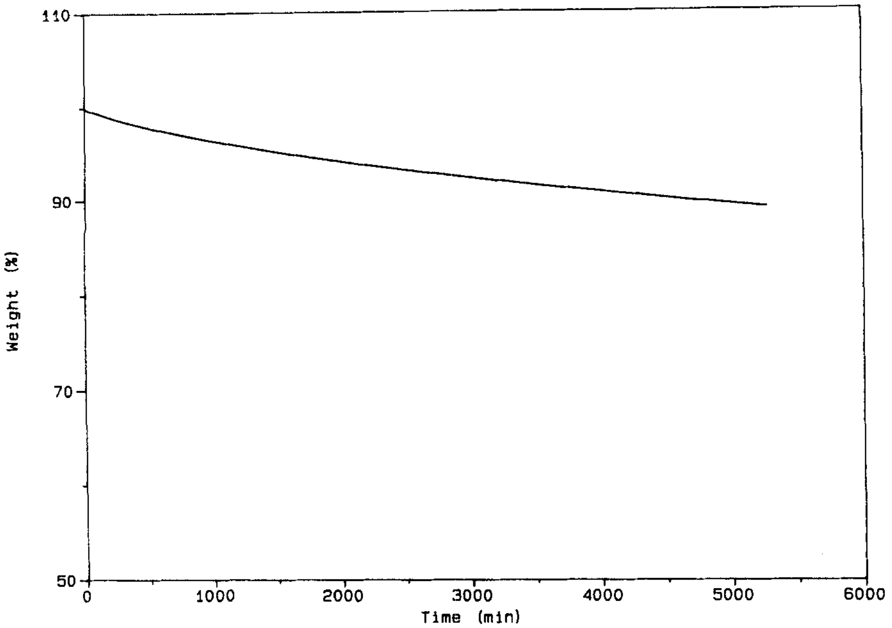

Fig. 1. Percent weight loss versus time curve for the reaction of zirconium fluoride monohydrate and ammonium bifluoride conducted isothermally at 30°C in a TGA. A mixture of 18.5 mg of ammonium bifluoride and 20 mg of zirconium fluoride monohydrate was used.

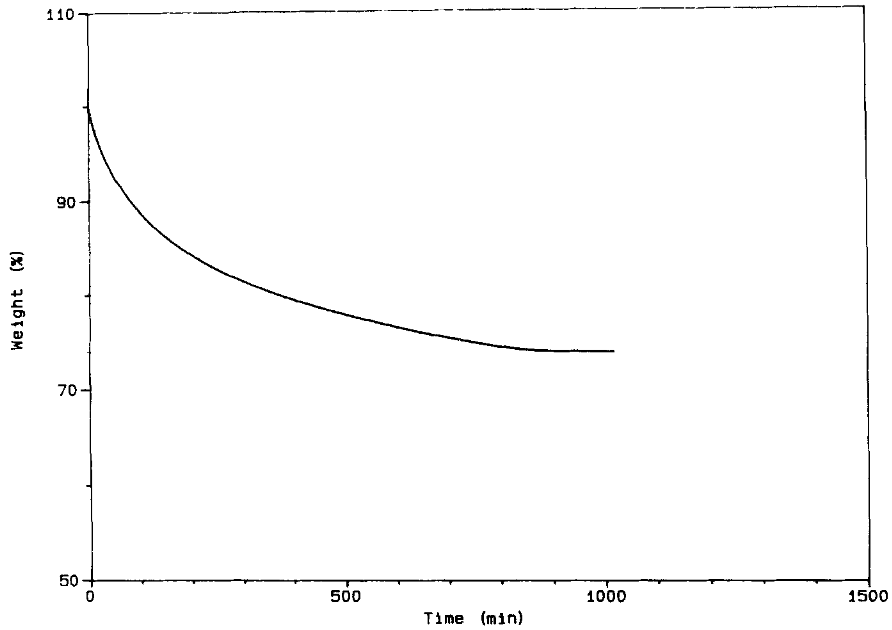

Fig. 2. Percent weight loss versus time curve for the reaction of zirconium fluoride monohydrate and ammonium bifluoride conducted isothermally at 70°C in a TGA. A mixture of 18.5 mg of ammonium bifluoride and 20 mg zirconium fluoride monohydrate was used.

hydrate or ammonium bifluoride present. In separate experiments, the weight loss due to elimination of hydrogen fluoride and water was monitored via a commercial thermogravimetric analyzer** (TGA). Two separate reactions were conducted isothermally at 30° and 70°C under flowing, gettered argon in the TGA. The weight loss versus time curves obtained from these reactions are shown in Figs. 1 and 2. A theoretical weight loss of 22% is calculated assuming the elimination of 1 mol of water and 3 mol of hydrogen fluoride, as shown by

$$ZrF_4{\cdot}H_2O(s) + 3NH_4F{\cdot}HF(s) \rightarrow (NH_4)_3ZrF_7(s) + H_2O(l) + 3HF(g) \quad (1)$$

Isothermal reaction at 30°C for 83 h yielded a total weight loss of 11%, which, based on the aforementioned theoretical calculation, indicates an incomplete reaction. However, when the reaction is conducted isothermally at 70°C for 18 h, the experimental weight loss of 25% slightly exceeds the theoretical weight loss, probably because of volatilization of some of the unreacted $3NH_4F{\cdot}HF$. Effectively, these data indicate that the reaction between zirconium fluoride monohydrate and ammonium bifluoride is complete in the TGA when conducted isothermally at 70°C after 18 h, whereas the isothermal reaction at 30°C never reaches completion, even after 3.5 d. Based on the data for the isothermal reaction at 70°C, the reaction sequence in Eq. (1) is implied. The respective products of the isothermal reactions at 30° and 70°C were subsequently heated to 900°C in the TGA under an argon atmosphere. The resulting weight loss versus temperature curves, as well as first derivative plots, are presented in Figs. 3 and 4, respectively. The first derivative plots in Figs. 3 and 4 have five and three distinct peaks, respectively. It is known that the thermal decomposition of zirconium fluoride monohydrate to anhydrous zirconium fluoride, oxyfluorides, or oxides occurs at 100° to 190°C and involves the elimination of hydrogen fluoride followed by water.[5,6] Additionally, ammonium bifluoride begins to sublime at 150°C, with almost 100% weight loss by 260°C. It is therefore evident that the first two peaks in Fig. 3 (30°C isothermal reaction), which are *not present* in Fig. 4 (70°C isothermal reaction), are most likely due to the elimination of water and hydrogen fluoride at 150°C, followed by the sublimation of unreacted ammonium bifluoride at 200°C. The three additional peaks at 220°, 275°, and 330°C evident in Figs. 3 and 4 are due to decomposition of the reaction products. Monitoring of the 70°C isothermal reaction for 18 h via TGA shows that most of the water and hydrogen fluoride are eliminated, indicating that the reaction has gone to completion.

Bragalia *et al.*[7] studied the high-temperature fluorination of zirconium oxide by ammonium bifluoride via differential scanning calorimetry and XRD. They report that the initial product formed at 150°C is $(NH_4)_3ZrF_7$, which decomposes to $(NH_4)_2ZrF_6$ at 140°C. Rodriguez *et al.*[8] showed that $(NH_4)_2ZrF_6$ decomposes in the following manner:

$$(NH_4)_2ZrF_6 \rightarrow (NH_4)ZrF_5 \qquad T = 212°C \quad (2)$$

$$(NH_4)ZrF_5 \rightarrow (NH_4)Zr_2F_9 \qquad T = 287°C \quad (3)$$

$$(NH_4)Zr_2F_9 \rightarrow ZrF_4 \qquad T = 347°C \quad (4)$$

Based on these data we tentatively assign the peaks obtained from both our TGA experiments as follows:

$$(NH_4)_2ZrF_7 \rightarrow (NH_4)_2ZrF_6 \qquad T = 220°C \quad (5)$$

$$(NH_4)_2ZrF_6 \rightarrow (NH_4)ZrF_5 \qquad T = 275°C \quad (6)$$

$$(NH_4)ZrF_5 \rightarrow ZrF_4 \qquad T = 330°C \quad (7)$$

As stated above, the peaks at 140° and 190°C, shown in Fig. 3 (30°C isothermal reaction), correspond to the elimination of water/hydrogen fluoride and the subliminaton of unreacted ammonium bifluoride, respectively. The formation/decomposition of $(NH_4)Zr_2F_9$ as reported by Rodriguez *et al.*[8] is not definitely observed in our work but may contribute to the fine structure evident in the first derivative plot of the decomposition at 330°C in both Figs. 3 and 4.

The significance of the reaction be-

**Model 951 DuPont Instruments, Wilmington, DE. TGA data were collected using a DuPont Instruments Thermal Analyst 2000 microprocessor system. The precision and accuracy for weight measurements are 0.4% and ±1.0% of full scale, respectively.

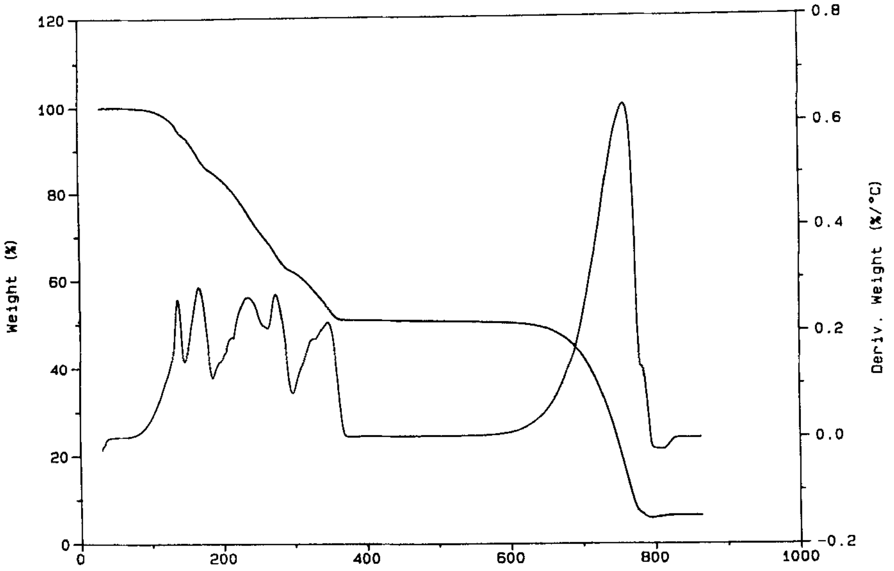

Fig. 3. TGA of ammonium bifluoride and zirconium fluoride monohydrate reaction product after isolation at 30°C for 18 h under flowing argon. Heating rate was 10°C/min.

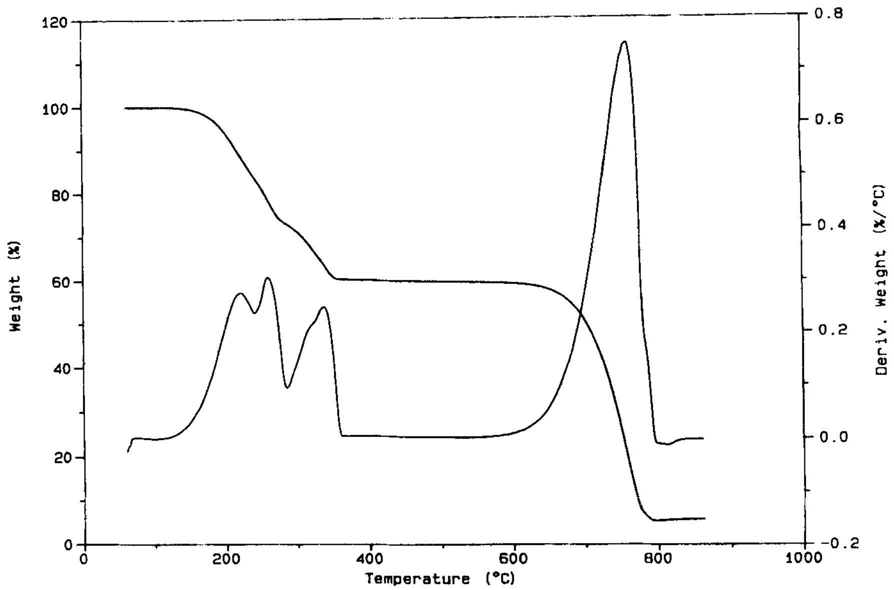

Fig. 4. TGA of ammonium bifluoride and zirconium fluoride monohydrate reaction product after isolation at 70°C for 18 h under flowing argon. Heating rate was 10°C/min.

tween zirconium fluoride monohydrate and ammonium bifluoride is quite clear when considering the quality of glass prepared via the processing route. When ammonium bifluoride is batched with the ZBLAN components, water and hydrogen fluoride are formed immediately because of the reaction between zirconium fluoride monohydrate and ammonium bifluoride. Fujiura *et al.*[9] recently showed that barium oxide, which is formed via high-temperature hydrolysis of barium fluoride, reacts in the melt with zirconium fluoride, forming zirconium oxide.

$$BaF_2+H_2O \rightarrow BaO+2HF(g) \quad (8)$$

$$ZrF_4+2BaO \rightarrow ZrO_2+2BaF_2 \quad (9)$$

The zirconium oxide formed is insoluble in the melt and will crystallize, forming scattering centers in the glass. Any free water in a ZBLAN batch will undoubtedly adsorb to the raw materials of the batch, providing a pathway for formation of oxides in the glass. The current study shows that ammonium bifluoride will react with zirconium fluoride monohydrate in a ZBLAN batch, producing free water as shown in Eq. (1). This free water can contribute to increased oxide formation via high-temperature hydrolysis of the ZBLAN glass components, subsequently leading to a less stable glass with more scattering centers.

However, based on our findings, ammonium bifluoride can be used to effectively dry zirconium fluoride monohydrate *before glass batching*. Low-temperature reaction of ammonium bifluoride with zirconium fluoride monohydrate prior to batching produces anhydrous ammonium heptafluorozirconate, $(NH_4)_3ZrF_7$. This material can then be batched with the other fluoride glass components for ZBLAN glass preparation. Additional ammonium bifluoride can be used to completely dry and fluorinate the other glass components if necessary.

We studied the reaction between ammonium bifluoride and zirconium fluoride monohydrate in bulk samples at 70°C for 18 h under flowing argon in order to produce a "dry" zirconium fluoride source. Our preliminary results indicate that we have eliminated the majority of water produced from the reaction shown in Eq. (1) prior to batching with other glass components. The ammonium heptafluorozirconate produced was then batched with the other ZBLAN components and melted to form a ZBLAN glass. Our initial study of this glass indicates that it is *at least* equal in quality to our best glasses made via direct batching of all materials. Although little or no evidence for crystallization has been found via optical microscopy, glasses prepared using ammonium heptafluorozirconate in place of zirconium fluoride monohydrate must be studied further to determine if these glasses are indeed of higher quality than those prepared via direct addition of ammonium bifluoride to the ZBLAN batch.

In conclusion, our initial study has shown that ammonium bifluoride is *not* an inert component of a fluoride glass batch but reacts with zirconium fluoride monohydrate at ambient temperatures, producing hydrogen fluoride and water. The presence of such free water is likely to increase scattering centers via high-temperature oxide formation. However, the pathway for introduction of water into the ZBLAN batch can be reduced, if not totally eliminated, via reaction of zirconium fluoride monohydrate and ammonium bifluoride prior to mixing with the other ZBLAN components. The product of this reaction, ammonium heptafluorozirconate, has been successfully melted into a ZBLAN fluoride glass.

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