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A PHENOMENOLOGICAL COMPARISON OF SOME HEAVY METAL FLUORIDE GLASSES IN WATER ENVIRONMENTS

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ABSTRACT

The details of corrosive attack by water on several heavy metal fluoride glasses are given. The glasses studied contain either ZrF_4 or HfF_4 as primary constituents, or, are composed of the fluorides of zinc, thorium, barium and either yttrium or ytterbium. Polished specimens were subjected either to room temperature (RT) liquid water or to 100% relative humidity at room temperature. The degree of surface corrosion is correlated to preparatory and compositional effects. Thermogravimetric analysis (TGA) was utilized to determine the extent of corrosion as a function of temperature and as a function of time at constant temperature in an atmosphere of RT helium saturated with water.

Introduction

A wide body of literature now exists relating to the preparation and physical properties of two relatively new types of non-oxide glass. The first of these, referred to here as "Type 1" glasses, are based on ZrF_4 or HfF_4 (1-6). Such glasses may be easily formed into colorless specimens several cm on a side by casting. The Type 1 glasses are continuously transparent from the UV to the mid-IR, are reasonably hard and strong, and are potentially useful as multispectral optical components, hot forged optical elements, IR domes, laser windows, laser hosts and fiber optic elements. Table 1 gives the physical properties of typical fluorozirconate (ZBT) and fluorohafnate (HBT) glasses of this kind, whose compositions represent the centers of their respective vitreous domains.

Table 1.

Physical Properties of ZBT and HBT Glass Prepared With a CCl_4 Reactive Atmosphere

10542-1R2

PROPERTIES	VALUES	
	ZBT	HBT
COMPOSITION	$Zr_{0.60}Ba_{0.33}Th_{0.07}F_{3.34}$	$Hf_{0.60}Ba_{0.33}Th_{0.07}F_{3.34}$
OPTICAL TRANSPARENCY	0.3 μm TO 7 μm	0.2 μm TO 8.5 μm
DENSITY	4.8 g/cm^3	6.2 g/cm^3
REFRACTIVE INDEX (n_D)	1.53	1.51
KNOOP HARDNESS (Kg-mm^{-2})	250	250
HEAT CAPACITY (C_p) AT 45°C	0.51 J/g-°C	0.43 J/g-°C
COEFFICIENT OF LINEAR EXPANSION		
30 TO 60°C	4.3×10^{-6}/°C	6.0×10^{-6}/°C AT 57°C
250 TO 270°C	13.8×10^{-6}/°C	6.2×10^{-6}/°C AT 227°C
RUPTURE STRENGTH	9,000 psi	9,000 psi
ABSORPTION COEFFICIENT AT HF LASER WAVELENGTH (2.8 μm)	6×10^{-3} cm^{-1}	
ABSORPTION COEFFICIENT AT DF LASER WAVELENGTH (3.8 μm)	2×10^{-3} cm^{-1}	

In addition, glass formation has recently been reported (7-13) in other fluoride systems devoid of either ZrF_4 or HfF_4. Glasses of this kind, termed "Type 2" in this work, typically contain BaF_2 and ThF_4 in conjunction with ZnF_2, YF_3 and/or YbF_3 and AlF_3. While many such compositions require rapid quenching to yield thin flakes of glass, others are sufficiently resistant to crystallization to allow preparation of castings several millimeters thick. Among the latter are glasses in the BaF_2-ZnF_2-YbF_3-ThF_4 (11-13) and BaF_2-ZnF_2-YF_3-AlF_3-ThF_4 (10) systems. Representative compositions prepared for this study, along with their acronyms, glass transition temperature, (Tg) and crystallization temperatures, (Tx) are shown in Table 2. Certain glasses of this type (e.g., BZnYbT) are of interest because their absorption coefficients in the 6-10 μm region are an order of magnitude lower than those typically observed in Type 1 glasses (12).

A prerequisite in many of the applications envisioned for heavy metal fluoride glasses is a resistance to attack from atmospheric moisture. This subject takes on significance in view of the hygroscopic nature of some of the fluoride constituents used in glass preparation. Simmons et al., recently reported the results of aqueous leaching tests carried out on both a Type 1 fluorozirconate glass (14) and a Type 2 glass (15) similar in composition to the BZnYbt glass of Table 2. Chemical analysis indicated that, on exposure to

Table 2.

Tg and Tx for Type 2 Glasses.

12917–1

COMPOUND	MOLE %		
	BZnYbT	BZnYbAT	BZnYAT
BaF_2	17.5	15	20
ZnF_2	26.5	27	29
YbF_3	26	27	
YF_3			14.4
AlF_3		4	14.4
ThF_4	30	27	22.2
Tg (°C)	350	354	355
T_x (°C)	428	459	494

liquid water, the individual constituents of each glass leached nearly congruently, resulting in formation of an opaque surface layer where fluorides have reverted to hydroxides. Type 2 glasses were observed to leach at a rate ~100 times lower than Type 2 glasses (15).

This paper attempts to elucidate the hydrolytic durability of both types of glasses in various water containing environments. Efforts are made to correlate the degree of surface corrosion with composition, preparatory conditions (e.g., use of reactive atmospheres), temperature, and relative humidity.

Experimental

Preparation

The Type 1 glasses employed in this study have the formula $M_{0.60}Ba_{0.33}R_{0.07}F_{3.34}$, where M = Zr or Hf and R = Th or La. The MF_4 was derived from either 99.9% HfO_2 (CERAC) or 99.5% ZrO_2 (CERAC) dissolved in aqueous 49% HF, evaporated to dryness and sublimed once to give colorless transparent needles of the desired product. ThF_4 and LaF_3 were prepared from 99.9% ThO_2 (CERAC) and 99.9% La_2O_3 (Research Chemicals Corp.). The oxides were also dissolved in aqueous HF and subsequently evaporated to dryness. The resulting fluorides were melted in a dry HF atmosphere (M.P. LaF_3 = 1495°C, M.P. ThF_4 = 1110°C). The BaF_2 was 99.99% pure from EM Labs. The starting materials were mixed with mortar and pestle, loaded into a vitreous carbon crucible and heated to melting (~800°C) in either a dry helium atmosphere or an atmosphere of gaseous CCl_4 (Mallinkrodt) diluted with helium. Glass batches weighed approximately 50 grams. At temperatures greater than 600°C CCl_4 is an effective reactive atmosphere (RA) for removal of OH^- in the melt, and perhaps even more importantly, it reacts with and removes the source of OH^-, namely, outgassed water according to the following

1. $CCl_{4(gas)} + 2OH^-_{(melt)} \rightleftarrows CO_{2(gas)} + 2Cl^-_{(melt)} + 2HCl_{(gas)}$

2. $CCl_{4(gas)} + 2\,H_2O_{(gas)} \rightleftarrows CO_{2(gas)} + 4HCl_{(gas)}$

Also, CCl_4 at the processing temperature pyrolytically cracks to give nascent chlorine (Cl) which not only eliminates OH^- impurities but has the added benefit of compensating for fluoride deficiencies in the final product. Utilization of CCl_4 gives very clear and transparent ingots of fluoride glass doped with about 1% Cl^- as revealed by electron microprobe analysis. The glass mixture is kept molten at 800°C for 3 hours, cooled abruptly to 300°C and annealed to remove strain.

Type 2 glasses were prepared using 99.9% or better BaF_2, ZnF_2, Yf_3, Yb_2O_3, AlF_3 and ThO_2 as raw materials. A large excess (4 times the stoichiometric amount) of ammonium bifluoride was mixed into each glass batch to ensure conversion of any oxide starting materials to fluorides. Glass melting was carried out in vitreous carbon crucibles under argon atmosphere in a resistance-heated furnace. After heating the batch to 400°C and holding for 1h to accomplish the oxide-fluoride conversion, the temperature was raised over a period of 4h to 950-1100°C. The clear liquid thus prepared was poured between two pre-heated (~250°C) brass blocks separated by 2-4 mm and annealed at 300°C overnight. Clear specimens ~1.5 cm x 3 cm resulted from this method.

Testing

Polished fluoride glass samples were subjected to water in the following way: For a time interval of 240 minutes, specimens were either maintained in direct contact with liquid water or situated in such a way that they continuously experienced 100% relative humidity at room temperature (RT). The TGA runs made use of a DuPont Model 1090 Thermal Analyzer console interfaced with a DuPont Model 910 TGA. Specimens were placed in platinum sample holders inside the TGA envelope. Interaction with water in a flowing stream of helium saturated with water vapor was measured as a function of time, holding temperature constant, and as a function of continuously increasing temperature from RT to ~1000°C at a preselected heating rate. Water saturation of the helium stream was accomplished by passing helium through a pyrex bubbler partially filled with RT deionized water.

Results and Discussion

Room Temperature Corrosion

Type 1 glasses are quite stable under room temperature laboratory environmental conditions of less than 100% relative humidity; polished and unpolished ingots show no visual signs of degradation or corrosion over several years exposure. However, under conditions of 100% relative humidity surface corrosion is rapid and severe. Figure 1 shows a polished disk of HBT glass (Table I) prepared in a CCl_4 reactive atmosphere. A sample such as this maintains its transparency indefinitely under normal conditions, but is rapidly attacked when treated with water.

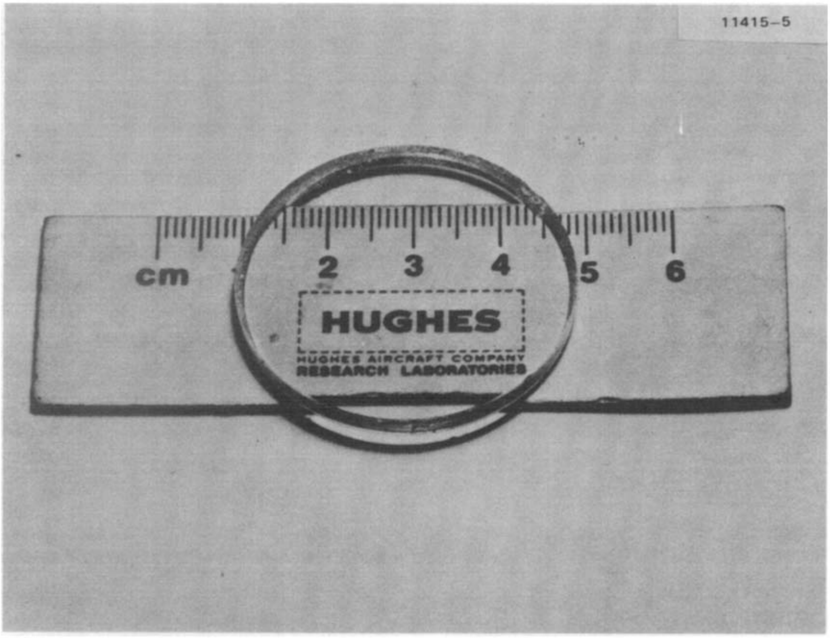

FIG. 1

HBT glass 4.5 mm thick.

Figure 2 shows the same specimen after cutting, processing and a water processing treatment which will now be described. The sections in the upper hemicircle are specified from left to right 1, 2, 3, 4, and 5. Sections 4 and 5 were first processed with gaseous anhydrous HF for one hour at 300°C in an attempt to passivate the surfaces to subsequent water treatment. Samples 1 and 5 were treated for 240 minutes at RT and 100% relative humidity then washed with isopropyl alcohol.

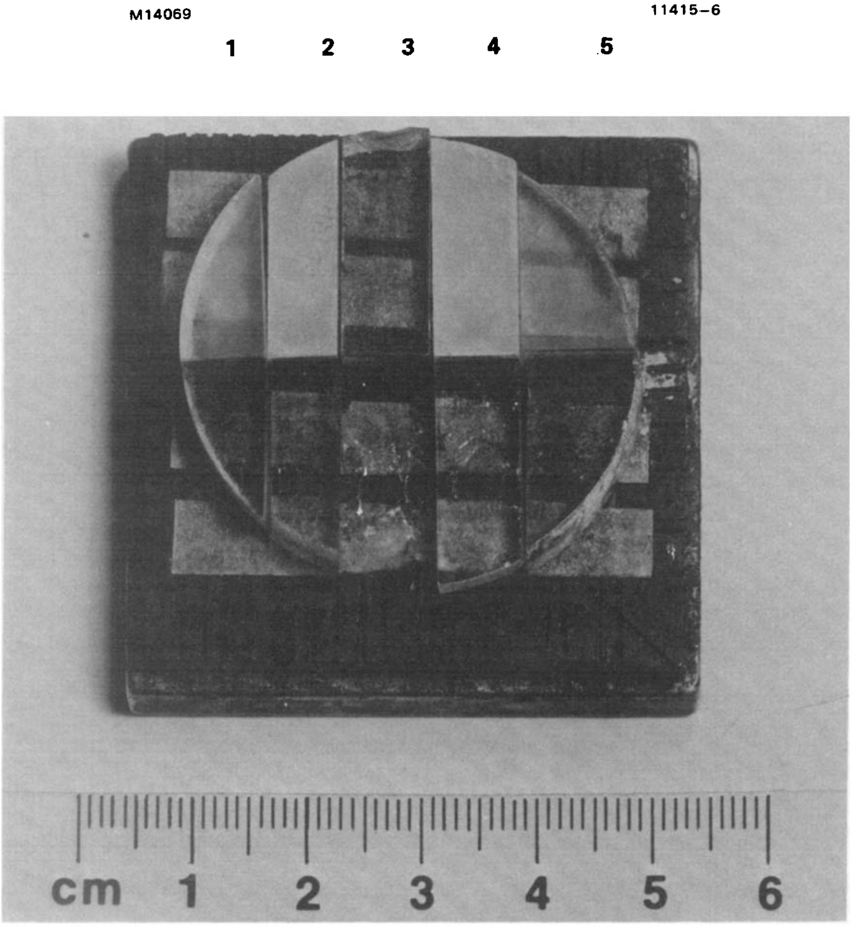

FIG. 2

HBT glass 4.47 mm thick.

Sample 3 was a control specimen. Conditions of 100% relative humidity were obtained by maintaining the samples in close proximity to a beaker of water inside a closed vacuum type dessicator. All samples were as clear and transparent as the control specimen, 3, prior to water processing. Note that the passivated specimen (#5) appears slightly more transparent than #1 which had no dry HF treatment after polishing. The IR spectra of these specimens as well as the control sample are given in Figure 3.

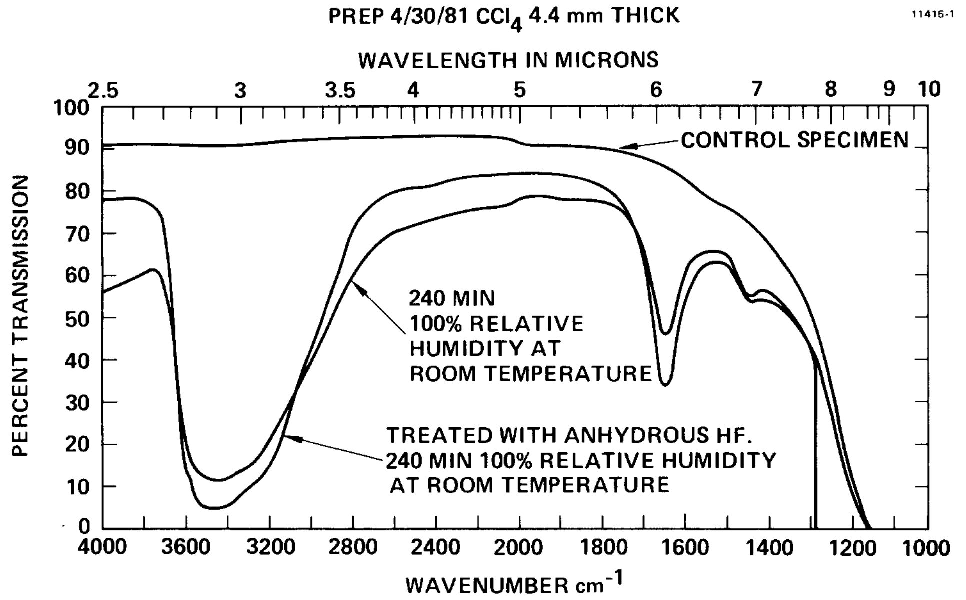

FIG. 3

Spectra HBT glass.

Absorptions due to OH^- streching mode at 3 microns and OH^- bending at ~6 microns, as well as a band in the vicinity of 7.0 microns, are very pronounced for both specimens. Simmons et al. have indicated that this latter band is due to oxide complexes which arise upon dehydration of samples whose surfaces have been attacked by water (14). Furthermore, these workers observed that such attack occurs only under conditions where liquid water, condenses on the specimens (as in the present experiment), and that the condition of 100% RH by itself is not a sufficient condition for corrosion. Samples repolished to a window-like finish duplicate the spectral properties of the control specimen (Figure 3), indicating that the corrosion is limited to a thin surface layer.

Samples 2 and 4 were covered with deionized water for 240 minutes at RT, removed and given a isopropyl alcohol wash. Both are significantly more opaque than samples subjected to 100% relative humidity for the same time period. The measured rates of dissolution for #2 and #4 using the 240 min data points are 7.5 x 10^{-6} g/cm^2/min and 10.0 x 10^{-6} g/cm^2/min, respectively These rates compare favorably with the value of 4.7 x 10^{-5} g/cm^2/min reported for a 57ZrF$_4$ - 34BaF$_2$ - 9ThF$_4$ glass subjected to boiling H_2O, although they are still ~10^3 times greater than those observed in typical silicate glasses (16).

Ternary fluorohafnate glasses may also be formed by completely replacing ThF$_4$ with LaF$_3$, yielding vitreous materials denoted here as "HBL". The resistance of HBL to water attack is considerably higher than HBT. Polished HBL specimens prepared under either CCl$_4$ or He and subjected to 240 min of room temperature 100% relative humidity showed only slight surface degradation. The IR spectra of these glasses are shown in Figure 4. An additional 390 min 100% relative humidity treatment rendered both HBL samples approximately as opaque when visually examined as the unpassivated HBT glass treated for 240 min (sample 1, Figure 2).

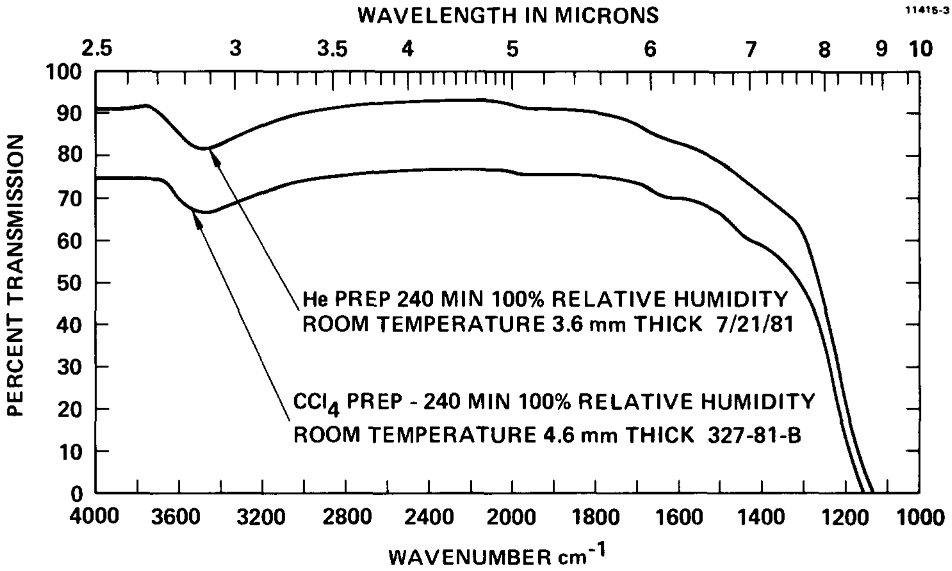

FIG. 4

Spectra HBL glass.

As suggested above, Type 1 glasses under the present experimental conditions absorb water on the surface. Absorption is followed by condensation and finally dissolution via the F^-/OH^- anion exchange described by Simmons et al. (14). In our case, X-ray power diffraction of the dissolved material recovered by vacuum drying showed it to be either a hydrated form of HfF_4 or $(HfF_4 \cdot HF)4H_2O$. That condensation is a necessary step in the low temperature corrosion process is seen in Figure 5 which shows 3 thermograms of HBT glass maintained at 50°C, 100°C, and 200°C. The samples consist of 1 or 2 submillimeter chips of glass. The atmosphere in each case is RT helium saturated with water vapor, and in each case corrosion is not detected since condensation is not possible. Microscopic examination of these samples after testing reveals no degradation or surface corrosion. TGA results for ZBT, HBL and HBT under isothermal conditions are given in Figure 6. The helium flow rates are the same for each sample. Note that the rate of water uptake for HBT far exceeds HBL or ZBT. Similar experiments with Type 2 glasses show virtually no water uptake and no degradation of any kind. The thermogram of a BZnYbT

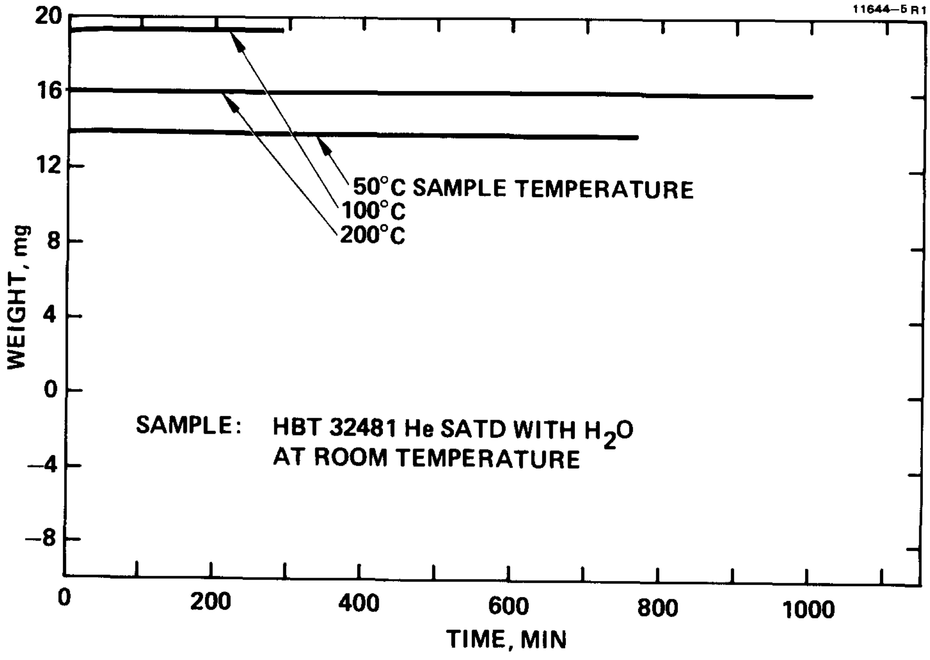

FIG. 5

TGA OF HBT

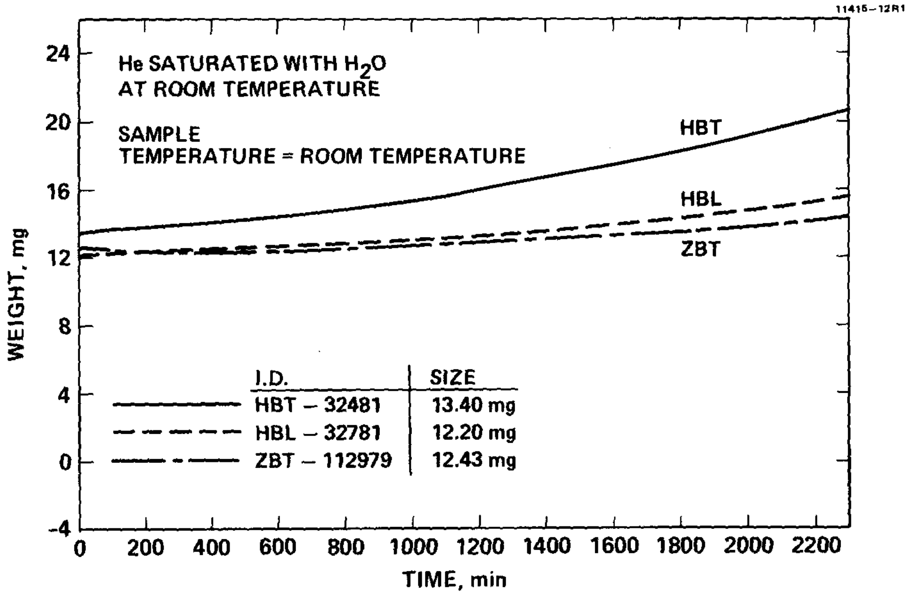

FIG. 6

TGA of fluoride glasses.

glass (Figure 7) illustrates this point, and is representative of data obtained for all of the Type 2 glasses in Table 2. No weight change is observed with time, indicating enhanced moisture resistance.

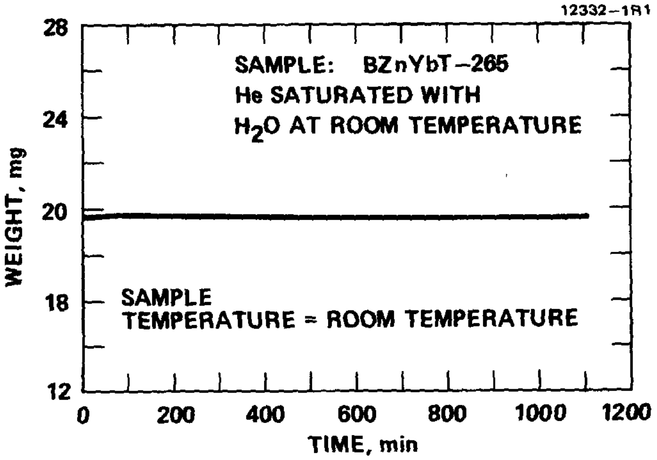

FIG. 7

TGA of BZnYbT-265.

Conclusions

All of the Type 1 and Type 2 heavy metal fluoride glasses tested are quite stable in normal environments over time periods measured in years. Under the testing conditions imposed, the Type 2 glasses exhibit a higher resistance to moisture attack than their fluorozirconate or fluorohafnate counterparts.

Type 1 glasses are attacked and begin to rapidly dissolve in liquid water. Attempts to passivate their surfaces via treatment with gaseous HF yielded no marked improvement. Under conditions approximating 100% relative humidity, e.g., RT helium saturated with water, these glasses show signs of surface degradation only when water can condense on the glass surface. If condensation is avoided, no corrosion is observed up to 200°C.

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