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FLUORIDE GLASS: CRYSTALLIZATION, SURFACE TENSION AND BUBBLES IN LOW GRAVITY

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ABSTRACT

Fluoride glass was levitated acoustically in the ACES apparatus on STS-11, and the recovered sample had a different microstructure from samples cooled in a container. Further experiments on levitated samples of fluoride glass are proposed. These include nucleation, crystallization, and melting observations, measurement of surface tension of molten glass, and observation of bubbles in the glass. Ground experiments are required on sample preparation, outgassing, and surface reactions. The results should help in the development and evaluation of containerless processing, especially of glass, in the development of a contaminent-free method of measuring surface tensions of melts, in extending knowledge of gas and bubble behavior in fluoride glasses, and in increasing insight into the processing and properties of fluoride glasses.

BACKGROUND

Fluoride Glass

A variety of fluoride glasses based on zirconium, hafnium or thorium fluoride are being intensively investigated because they are transparent in the infrared to 8 μm and beyond.[1-4] Optical components such as lenses, prisms, and fibers for use in the infrared can be made of these glasses. An especially attractive application envisions fiber optic wave guides for long distance communication. Fibers of vitreous silica are already being used for this purpose. The length of each link in a communication chain is limited by optical scattering and absorption; silica has a minimum combined absorption at about one μm. The fluoride glasses have in theory a much deeper minimum than silica at longer wavelengths because their absorption edge is further into the infrared. Much progress has been made in forming fibers for these purposes and reducing their absorption and scattering losses.

Optical fibers are being investigated as sensors for a wide variety of environmental factors, including temperature, pressure, displacement, acoustic field, electromagnetic waves, and even composition.[8] Availability of glasses with wider ranges of transparency in the infrared should provide new and improved sensors.

These fluoride glasses satisfy the requirements of high value and low volume materials for space processing. If different compositions with a larger range of infrared transparency could be made because of the reduced contamination and wall nucleation during containerless processing, many more valuable glasses would be available.

These fluoride glasses are made by melting the constituent fluorides together with ammonium bifluoride ($NH_4F \cdot HF$) in a vitreous carbon crucible in an atmosphere of 3% chlorine in dry nitrogen. A composition extensively studied, and the one used for the shuttle experiment, is 62 mole% ZrF_4, 33% BaF_2 and 5% LaF_3, designated as ZBL glass. A maximum temperature of about 900°C was required to ensure complete melting. The molten glass was cast into brass or steel molds, annealed near the glass transition temperature of about 320°C, and cooled slowly to room temperature. Spheres of glass were cast for flight experiments; they contained a bubble of entrapped air.

The crystallization and melting of ZBL and many other fluoride glasses were studied with differential scanning calorimetry (DSC), X-ray diffraction, and the scanning electron microscope.[5-7] Surface crystallization leads to crystals about 10 µm in size and a peculiar wrinkling of the surface.[6] In ZBL glass the crystalline phases that form are $BaZrF_6$ and BaZ_2F_{10}; each of these phases has two polymorphs.[5] In ZBL glass fine crystals grow spherically in the glass volume when it is heated in the DSC_5; when the glass melt is cooled slowly, large columnar crystals are nucleated on the container walls and grow into the melt, as shown in Fig. 14, App. I.

These columnar crystals were not found in a crystallized sample from the shuttle flight, shown in App. I. This sample was levitated in the furnace in the field of view up to about 450°C, when it was lost from view for the rest of the flight. It is possible that the sample stuck to a portion of the wire holding cage, because one piece of the sample had a dark rim or line depression on it, perhaps from contact with the cage. Thus crystallization on cooling from the molten condition probably took place more uniformly and on a smaller scale than if the sample crystallized from a crucible. More experiments are needed to test these possibilities. The post-flight analysis of the sample is described in a report attached as an appendix.

It seems likely that the columnar crystals of Fig.14 are caused by nucleation on the wall of the platinum crucible, and heat flow from the melt to the cooler wall. The absence of a container for a levitated sample precludes this mechanism of crystallization, and should lead to a more uniform fine crystallization thoughout the sample volume. This kind of uniform nucleation should require a greater undercooling, and so should occur only at slower cooling rates as compared to the crystallization nucleated on the crucible wall. More experiments on levitated samples are needed to test these possibilities.

The solubilities, diffusion coefficients, and reactivities of gases in fluoride glasses are poorly known. Gases in these glasses can influence processing, including fining (removal of bubbles), formation of defects, crystallization rates, and chemical reactivity. Vaporization rates and vaporized species have been little studied. Further knowledge of gaseous behavior in fluoride glasses is essential to control processing, fining, crystallization, and defect formation.

Containerless Processing

The possibility of making and studying liquid and solid materials without a container has exciting potential for increased learning about these materials. For glasses the advantages of purity and reduction of nucleation by the container could lead to new compositions and methods of forming.

Various ways of holding levitated samples in position are being explored. Acoustic levitation is particularly attractive because it can be used for any kind of sample and position controlled by the geometry of the system and the power fed to the acoustic drivers. A three-axis acoustic levitator (ACES) has been designed and built at the Jet Propulsion Laboratory (JPL), and was used to levitate a one cm. sphere of fluoride glass in shuttle flight STS-11. A single-axis acoustic levitator is being developed under the supervision of Marshall Space Flight Center. Air jet levitators are also being built and tested, and electrostatic levitation is possible for a dielectric sample. It will require much further testing to determine which systems are optimum for levitating different materials of interest at different conditions of temperature and atmosphere.

Surface Tension

The surface tension of high-temperature melts is usually measured by a sessile or pendant drop experiment.[9,10] However, the surface tension of a liquid can be strongly influenced by contamination with impurities, and these methods require that the drop rest on a substrate or be held by a tube or rod. If the melt is reactive, there is also a possibility of contamination from these foreign materials. Thus it would be highly desirable to find a method of measuring surface tension of a levitated melt at high temperatures. The vibration of a drop depends on its surface tension, so the vibration of a levitated drop, excited by an acoustic field, can be used to measure its surface tension. This method is being developed at JPL by Drs. Taylor Wang and Daniel Elleman and their colleagues, and has been successful for drops at room temperature.

Bubble Motion and Shrinkage

One of the most difficult steps in preparing glass, especially for optical purposes, is to remove bubbles in the viscous melt. In commercial practice bubbles are removed both by expanding and rising to the glass surface and by shrinking.[11-13] However, in low gravity bubbles will not "rise", and their motion and growth or shrinkage are important factors in making a bubble-free glass.

Diffusion of gas into the glass appears to control bubble shrinkage in most glasses.[11,12,14] Complete mathematical solutions to the problem of diffusion-controlled shrinkage of a bubble are difficult, so a variety of approximation methods have been used.[11-15] Weinberg and his collaborators have explored a variety of conditions and solutions of bubble growth and shrinkage equations (see refs. 15 and 16 and references therein). From these equations it is possible to calculate diffusion coefficients and solubilities of gases in melt from the rate of shrinkage of a gas bubble in the melt. Thus measurements of bubble shrinkage rates can give valuable information on processing of glass and on the properties of gases in the glass. A levitated drop has the advantage that the bubble is likely to be stationary, giving relatively simple mathematical boundary conditions Effects of convection are reduced in low gravity; these effects could be important in the relatively fluid melts of the fluoride glasses.

PROPOSED FLIGHT EXPERIMENTS

Crystallization and melting experiments on a levitated sphere of ZBL glass are proposed. The glass will be heated at a constant rate of from five to twenty degres per minute from the glass transition temperature of about 300°C up to a temperature (about 600°C) when the glass is completely molten. The nucleation and growth of crystalline phases and their melting will be observed during the heating. After the sample is held for several (up to 30) minutes at 600°C for the surface tension experiment, it will be cooled in the furnace at a rate similar to the heating rate. Again the nucleation and growth of crystalline phases will be observed. When the sample is completely crystallized (below about 450°C) it will be captured by a restraining cage, so it will hold together for post-flight analysis.

Surface tension of the glass melt will be measured from the vibrating molten sample, excited by the acoustic field. This experiment is being developed by Dr. Dan Elleman and his colleagues at JPL. They have measured surface tensions of levitated liquid drops at room temperature by this method. The details of this method are discussed in a memorandum by Dr. Elleman; a copy is included as an appendix to this proposal. If the viscosity is low enough, the frequency w_n of an osciallting drop in the nth mode is given by:

$$w_n^2 = n(n-1)(n+2)\sigma/\rho R^3 \qquad (1)$$

where σ is the surface tension, ρ is the density, and R the radius of the drop. The viscosity of the fluoride glass at 620°C is apparently low enough for this equatiodn to be valid.

Changes in the size and position of an air bubble in the sample will be observed throughout the heating and cooling cycle. The rate of growth or shrinkage of the bubble will give some information on the solubility anbd diffusion of gases in the glass; a complete interpretation of such results would require extensive ground-based experiments to determine these quantities for comparison with zero gravity results. Such experiments are not part of this proposal. Bubble motion should indicate flow in the glass, if any, and forces such as gravitational, thermal, and surface tension. Again a complete analysis would probably require extensive ground experiments.

Post-flight analysis of the sample will include chemical analysis, microscopic analysis in the SEM, and X-ray diffraction. The results from the experiment on STS-11 showed (from EDS analysis on the SEM) that the sample had the same zirconium-to-barium ratio as the starting glass, and that the crystalline phases were mostly $BaZrF_6$ and $BaZr_2F_{10}$, which are the same phases found when the fluoride glass crystallizes on heating, and upon cooling from the melt, on the ground. However, the proportions of the various α and β polymorphs of these phases of the levitated sample were different from those found in a crystallized glass cooled slowly from the melt. The microstructures of the space and ground samples were also quite different, as shown in the report included as Appendix I. Additional work is proposed to give more information on differences between samples cooled in the levitated condition and in a crucible.

EQUIPMENT

The experiments on fluoride glass in flight STS-11 were carried out in the ACES equipment built at JPL. Most aspects of this equipment functioned well, for example, the computorized controls and the furnace. However, there were two factors that need improvement if the proposed experiments are to be carried out successfully in this equipment. These are the viewing capability and the sample stability. The engineering group at JPL is working on improving these factors and ground tests are planned to see if the improvements are adequate. Additional discussion of the equipment and its functioning is given in Appendix I.

As part of the cooperation with JPL for the STS-11 experiment, a small Science Working Team was established to help in developing the ACES equipment and the experiment. Engineering and scientific personnel from JPL met with two outside members (Prof. S. Subramanian, Clarkson, and Dr. Ray Downs, KMS Fusion) and Prof. R. H. Doremus as Chairman. This group was very important in the success of the experiment, because it provided close, critical cooperation between the Principal Investigator for the experiments (Prof. Doremus) and the engineers and scientists at JPL. The two outside members gave critical, objective help throughout. A continuation of a similar group for any future experiments is proposed.

GROUND-BASED EXPERIMENTS

Preparation of spherical samples of fluoride glasses for the flight experiments will be continued. An especially important problem is outgassing of samples as they are heated. (See report in Appendix I.) During the flight experiment the viewing became rapidly more cloudy as the sample was held at 600°C. Apparently the alumina window was etched by a corrosive gas, which was probably hydrofluoric acid from the sample. The fluoride glasses are melted in an excess of ammonium bifluoride ($NH_4F\cdot HF$) to convert any oxide impurities to fluorides, and it is quite possible that some HF is retained in the glass after it is quenched.

Fluoride glasses will be melted with purified starting materials without ammonium bifluoride, and samples will be tested for gaseous products up to 650°C. Outgassing will be followed with weight change in a sensitive microbalance (Cahn), and gases emitted will be analyzed by mass spectrometry. The reactivity of the glass with inconel alloy, the material of construction of the ACES furnace, will also be studied.

The vaporization of zirconium fluoride, perhaps after reaction with water vapor, is another possible source of HF:

$$ZrF_4 + 2H_2O_{(g)} = ZrO_2 + 4HF_{(g)} \tag{2}$$

At room temperature, the standard free energy change for this reaction is about +52 kj/mole, so it is unfavorable; however, at 625°C it is about -106 kj/mole. Thus at the melt temperatures reaction 2 is quite favorable, and any small amount of water in the sample or system will react with the glass to form HF gas.

When the fluoride glass is heated in humid air to about 600°C, where it is molten, a white film forms on the surface, probably composed of zirconium oxide from reaction 2; in dry nitrogen the film is absent. More experiments on the reaction of water and other gases such as chlorine, used in the melting of the glasses, are proposed to determine surface condition and reaction products. A surface unreactive to water can form on the fluoride glass,[17] and its nature will be investigated.

There have been several investigations of the reaction of liquid water with the fluoride glass[18-20]; our work will continue with support from the National Science Foundation.

SIGNIFICANCE OF THE WORK

The main goal of this work is to develop the capabilities of containerless processing, especially of glasses. The experiments on nucleation, crystallization and melting will help to show whether or not there are advantages in containerless processing for making new glass compositions, and to gain more insight into the role of containers, gravity, and convection in these processes. The measurement of surface tension of levitated samples should be valuable for reactive melts and those highly sensitive to contamination. Growth, shrinkage, and motion of bubbles in the glass melt in low gravity should show the importance of convection and forces low compared to gravity on these processes. The experiments should also give considerable additional information in these areas for fluoride glasses, which show great promise for applications as otpical components, especially fiber-optic wave guides.

REFERENCES

1. M. Poulain, M. Chanthanasinh and J. Lucas, Mater. Res. Bull. 12, 151 (1977).

2. C. T. Moynihan, M. G. Drexhage, B. Bendow, M. Saleh-Boulos, K. P. Quinlan, K.-H. Chung, and E. Gbogi, ibid 16, 25 (1981).

3. M. Drexhage et al. and S. Takahashi et al. in "Physics of Fiber Optics", B. Bendow and S. S. Mitra, eds., Am. Ceramic Soc., Columbus, Ohio, 1981, pp. 57-73, 74-83.

4. C. M. Baldwin, R. M. Almeida and J. D. Mackenzie, J. Noncryst. Solids 43, 309 (1981).

5. N. P. Bansal, R. H. Doremus, A. J. Bruce and C. T. Moynihan, J. Amer. Cer. Soc. 66, 233 (1983); Mat. Res. Bull. 19, 577 (1984); to be published.

6. N. P. Bansal and R. H. Doremus, J. Amer. Cer. Soc. 66, C-132 (1983).

7. M. C. Weinberg, G. F. Neilson and G. L. Smith, J. Noncryst. Solids 56, 45 (1983); Mat. Res. Bull., (1984).

8. "Seminar on Optical Fiber Sensors", Amer. Cer. Soc. Bull. 63, 496 (1984).

9. J. K. Davis and F. E. Bartell, Anal. Chem. 20, 1182 (1948).

10. A. W. Adamson, "Physical Chemistry of Surfaces", John Wiley, New York (1976), p. 28ff.

11. C. H. Greene and R. F. Gaffney, J. Amer. Chem. Soc. 42, 271 (1959).

12. R. H. Doremus, ibid 43, 655 (1960).

13. M. Cable, Glass Tech. 2, 60 (1961).

14. R. B. Brown and R. H. Doremus, J. Am. Cer. Soc. 59, 510 (1976).

15. M. C. Weinberg, P. J. K. Onorato and D. R. Uhlmann, ibid, 63, 175, 435 (1980); 64, 676 (1981).

16. R. S. Subramaniam and M. C. Weinberg, AIChEJ 27, 739 (1981).

17. C. Burman, W. A. Lanford, R. H. Doremus, and D. Murphy, Appl. Phys. Lett. 44, 845 (1984).

18. C. J. Simmons, H. Sitter, J. H. Simmons and D. C. Tran, Mat. Res. Bull. 17, 1203 (1982).

19. S. Mitachi, Phys. Chem. Glasses 24, 146 (1983).

20. R. H. Doremus, N. P. Bansal, T. Bradner and D. Murphy, J. Matls. Sci. Lett. 3, 484 (1984).