STABLE COMPOSITIONS FOR FLUORIDE GLASSES

P. K. Gupta
Department of Ceramic Engineering

For the Period
January 1, 1988 - March 31, 1988

NAVAL RESEARCH LABORATORY
Washington, D.C. 20375

Contract No. N00014-87-C-2186

OSU
The Ohio State University
Research Foundation
1314 Kinnear Road
Columbus, Ohio 43212
REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
   Unclassified

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3 DISTRIBUTION/AVAILABILITY OF REPORT
   Approved for Public Release
   Distribution Unlimited

4 PERFORMING ORGANIZATION REPORT NUMBER(S)
   RF Project 766261/719844

6a. NAME OF PERFORMING ORGANIZATION
   The Ohio State University Research Foundation

6b. OFFICE SYMBOL
    OSURF

7a. NAME OF MONITORING ORGANIZATION

7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
   Naval Research Laboratory

8b. OFFICE SYMBOL
    (if applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
   Contract # N00014-87-C-2186

10. SOURCE OF FUNDING NUMBERS
    PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT NO.

11. TITLE (Include Security Classification)
    Stable Compositions for Flouride Glasses

12. PERSONAL AUTHOR(S)
    P. K. Gupta

13a. TYPE OF REPORT
    Technical

13b. TIME COVERED
    FROM 1/1/88 TO 3/31/88

14. DATE OF REPORT (Year, Month, Day)
    1988/April

15. PAGE COUNT
    7

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
    □ UNCLASSIFIED/UNLIMITED □ SAME AS RPT □ DTIC USERS

22a. NAME OF RESPONSIBLE INDIVIDUAL
    P. K. Gupta

22b. TELEPHONE (Include Area Code)
    (614) 292-6769

22c. OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete.

UNCLASSIFIED
STABLE COMPOSITIONS FOR FLUORIDE GLASSES

P. K. Gupta
Department of Ceramic Engineering

For the Period
January 1, 1988 - March 31, 1988

NAVAL RESEARCH LABORATORY
Washington, D.C. 20375

Contract No. N00014-87-C-2186

April 1988
Introduction

This research contract is part of the NRL effort to produce ultralow-loss long-length fluoride glass fibers. A previous report described the work done in 1987. This interim report describes the progress in the first quarter of 1988.

Objectives of the Project

There are two distinct objectives:

1. Composition Search
   - To explore new fluorozirconate glass compositions more stable than the current composition in use at NRL.

2. Process Modeling
   - To determine the relative influences of various material and process parameters on the crystals in preforms and fibers.

Results

1. A completely enclosed facility to melt halide glasses in controlled environments (principally Argon and oxygen) has been successfully completed. Reference ZBLAN composition was melted successfully many times to optimize the melting procedure (i.e., the amount of ammonium bifluoride, the flow rate of Argon, and the use of oxygen at the end of melting). The optimized melting schedule is described in Appendix I.

2. Several new compositions have been melted. Table I lists these compositions. Each composition has been melted at least two times.

3. Table II summarizes the optical quality of the bulk glass samples. From these results it appears that the stable glass forming region extends (starting from the reference composition)
   (i) at least 4 mole % towards the ZrF$_4$ direction,
   (ii) less than 4 mole % towards the BaF$_2$ direction, and
   (iii) less than 4 mole % towards the LaF$_3$ direction.

4. Computer modeling of the preform-making process is being carried out following the strategy and procedure which was described in detail in the previous report. Modeling has been completed for Phase I, which consists of solving two coupled non-linear equations for the case of a cylinder (i) heat equation (modified to include the latent heat of crystallization as a heat source term) with convective boundary conditions, and (ii) the equations for nucleation and growth kinetics.
5. The input parameters include material parameters (including those appearing in the theory of classical nucleation and growth -- again see details in the previous report) and several process parameters (radius of preform, heat transfer coefficient, initial temperature of melt). The values of these parameters and the reasons for choosing these values are described in detail in the previous report. However, the values can be readily adjusted when better data become available.

6. The output of the program gives as a function of time of cooling:
   (i) temperature as a function of radial position,
   (ii) volume fraction of crystals as a function of radial position,
   (iii) maximum size of crystal and the number density of crystals as a function of radial position, and
   (iv) the overall volume fraction of crystals in the cylinder.

7. The program has been successfully tested for internal consistencies, for consistencies of the output data, and for the stability of the solution against discretization of the equations (inherent in numerical analysis) and round-off errors.

8. The key modeling results thus far include:
   (i) the temperature may not decrease monotonically with time as a consequence of the heat of crystallization, and
   (ii) volume fraction of crystals is extremely sensitive to the ratio of thermal conductivity of the melt and the product of the heat transfer coefficient and preform radius. Some of these results were discussed with Drs. Aggarwal and Lu recently. Details of these results will be given in the next report.

Plans for April 1988 through June 1988

1. Finish exploration of ZBLAN system (May 15, 1988).
2. Investigate the effect of substitution of K for Na (June 1, 1988).
3. Examination of optical quality (June 15, 1988).
4. Use of simplex optimization technique to determine the best composition (June 15, 1988).
5. Model the crystallization behavior of preform as a function of
   (a) time dependent heat transfer coefficient (May 15, 1988), and
   (b) important material parameters (June 15, 1988).
Table I. ZBLAN Compositions

(Mole %)

<table>
<thead>
<tr>
<th></th>
<th>ZrF₄</th>
<th>BaF₂</th>
<th>LaF₃</th>
<th>AlF₃</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z₁</td>
<td>57.00</td>
<td>18.29</td>
<td>3.66</td>
<td>2.74</td>
<td>18.30</td>
</tr>
<tr>
<td>Z₂</td>
<td>61.00</td>
<td>16.60</td>
<td>3.32</td>
<td>2.49</td>
<td>16.60</td>
</tr>
<tr>
<td>Z₃</td>
<td>65.00</td>
<td>14.89</td>
<td>2.98</td>
<td>2.23</td>
<td>14.89</td>
</tr>
<tr>
<td>Z₄</td>
<td>69.00</td>
<td>13.19</td>
<td>2.64</td>
<td>1.98</td>
<td>13.19</td>
</tr>
<tr>
<td>B₁</td>
<td>50.35</td>
<td>24.00</td>
<td>3.80</td>
<td>2.85</td>
<td>19.00</td>
</tr>
<tr>
<td>B₂</td>
<td>47.70</td>
<td>28.00</td>
<td>3.60</td>
<td>2.70</td>
<td>18.00</td>
</tr>
<tr>
<td>B₃</td>
<td>45.05</td>
<td>32.00</td>
<td>3.40</td>
<td>2.55</td>
<td>17.00</td>
</tr>
<tr>
<td>B₄</td>
<td>42.40</td>
<td>36.00</td>
<td>3.20</td>
<td>2.40</td>
<td>16.00</td>
</tr>
<tr>
<td>L₁</td>
<td>50.79</td>
<td>19.17</td>
<td>8.00</td>
<td>2.88</td>
<td>19.17</td>
</tr>
<tr>
<td>L₂</td>
<td>48.58</td>
<td>18.33</td>
<td>12.00</td>
<td>2.75</td>
<td>18.33</td>
</tr>
<tr>
<td>L₃</td>
<td>46.38</td>
<td>17.50</td>
<td>16.00</td>
<td>2.62</td>
<td>17.50</td>
</tr>
<tr>
<td>L₄</td>
<td>44.17</td>
<td>16.67</td>
<td>20.00</td>
<td>2.50</td>
<td>16.67</td>
</tr>
<tr>
<td>A₁</td>
<td>50.81</td>
<td>19.18</td>
<td>3.84</td>
<td>7.00</td>
<td>19.18</td>
</tr>
<tr>
<td>A₂</td>
<td>48.63</td>
<td>18.35</td>
<td>3.67</td>
<td>11.00</td>
<td>18.35</td>
</tr>
<tr>
<td>A₃</td>
<td>46.44</td>
<td>17.53</td>
<td>3.51</td>
<td>15.00</td>
<td>17.53</td>
</tr>
<tr>
<td>A₄</td>
<td>44.26</td>
<td>16.70</td>
<td>3.34</td>
<td>19.00</td>
<td>16.70</td>
</tr>
<tr>
<td>N₁</td>
<td>50.35</td>
<td>19.00</td>
<td>3.80</td>
<td>2.85</td>
<td>24.00</td>
</tr>
<tr>
<td>N₂</td>
<td>47.70</td>
<td>18.00</td>
<td>3.60</td>
<td>2.70</td>
<td>28.00</td>
</tr>
<tr>
<td>N₃</td>
<td>45.05</td>
<td>17.00</td>
<td>3.40</td>
<td>2.55</td>
<td>32.00</td>
</tr>
<tr>
<td>N₄</td>
<td>42.40</td>
<td>16.00</td>
<td>3.20</td>
<td>2.40</td>
<td>36.00</td>
</tr>
<tr>
<td>B-1</td>
<td>55.65</td>
<td>16.00</td>
<td>4.2</td>
<td>3.15</td>
<td>21.00</td>
</tr>
<tr>
<td>B-2</td>
<td>58.30</td>
<td>12.00</td>
<td>4.4</td>
<td>3.3</td>
<td>22.00</td>
</tr>
<tr>
<td>L-1</td>
<td>54.10</td>
<td>20.42</td>
<td>2.0</td>
<td>3.063</td>
<td>20.42</td>
</tr>
<tr>
<td>L-2</td>
<td>55.20</td>
<td>20.84</td>
<td>0.0</td>
<td>3.126</td>
<td>20.842</td>
</tr>
</tbody>
</table>

* compositions studied
** compositions ruled out from study
Table II. Optical Quality of Bulk Glass Samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Visual Grade (VC,M,R,VB)</th>
<th>Optical Grade</th>
<th>Top Surface Crystal Grade (G,M,R,VB)</th>
<th>Bottom Surface Crystal Grade (VG,G,M,R,VB)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF 3-7-88</td>
<td>C-M</td>
<td>A1</td>
<td>B</td>
<td>VB</td>
<td>Many bubbles in bulk-10 per field of view.</td>
</tr>
<tr>
<td>REF 3-10-88</td>
<td>C</td>
<td>A1 below .6mm</td>
<td>M</td>
<td>M</td>
<td>Bow ties, hexagons, and ellipses present.</td>
</tr>
<tr>
<td>REF 3-16-88</td>
<td>VC</td>
<td>A1</td>
<td>G-M</td>
<td>VG</td>
<td>Best sample.</td>
</tr>
<tr>
<td>REF 3-25-88</td>
<td>C</td>
<td>A1</td>
<td>B</td>
<td>M</td>
<td>Bow ties and hexagons present.</td>
</tr>
<tr>
<td>Z1</td>
<td>VC</td>
<td>A1 below .6mm</td>
<td>M</td>
<td>VG</td>
<td>Cannot determine X-stal shape.</td>
</tr>
<tr>
<td>Z1</td>
<td>C</td>
<td>A1-2</td>
<td>M</td>
<td>M</td>
<td>One side of glass plug is noticeably more crystallized.</td>
</tr>
<tr>
<td>Z2</td>
<td>C</td>
<td>A3</td>
<td>R</td>
<td>M</td>
<td>Crystals preferentially oriented radially.</td>
</tr>
<tr>
<td>Z2</td>
<td>C</td>
<td>A1</td>
<td>M</td>
<td>M</td>
<td>Ellipse, bow ties, and flower crystals present.</td>
</tr>
<tr>
<td>Z2</td>
<td>C</td>
<td>A6S</td>
<td>B</td>
<td>M</td>
<td>Few bubbles on bottom, small crystals ruined rating.</td>
</tr>
<tr>
<td>Z3</td>
<td>C-M</td>
<td>A65</td>
<td>B</td>
<td>B</td>
<td>Better than 4-4-88, most crystals are very large.</td>
</tr>
<tr>
<td>Z4</td>
<td>M-B</td>
<td>A4L</td>
<td>B</td>
<td>B</td>
<td>Bulk crystals large 200u, difficult to rate.</td>
</tr>
<tr>
<td>B1</td>
<td>B</td>
<td>A5</td>
<td>VB</td>
<td>B</td>
<td>Top half fairly good glass, bottom half crystallized.</td>
</tr>
<tr>
<td>B2</td>
<td>VB</td>
<td>A10</td>
<td>VB</td>
<td>VB</td>
<td>Totally crystallized.</td>
</tr>
<tr>
<td>B2</td>
<td>VB</td>
<td>A10</td>
<td>VB</td>
<td>B</td>
<td>Totally crystallized.</td>
</tr>
<tr>
<td>L1</td>
<td>4-14-88</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>Bottom half totally crystallized.</td>
</tr>
<tr>
<td></td>
<td>VC = Very Clear</td>
<td></td>
<td>VG = Very Good</td>
<td>S = Small Crystals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C = Clear</td>
<td></td>
<td>G = Good</td>
<td>L = Large Crystals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M = Medium</td>
<td></td>
<td>M = Medium</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B = Bad</td>
<td></td>
<td>B = Bad</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VB = Very bad</td>
<td></td>
<td>VB = Very Bad</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix I
Melting Procedure

1. Weigh constituents and mix.
2. Weigh and mix NH₄HF₂ to batch in crucible.
3. Place batch in melting apparatus and seal tube.
4. Adjust Ar to .3 l/min for first 45 minutes then reduce to .1 l/min. just to ensure atmosphere.
5. After 6.25 hours change atmosphere to oxygen at .3 l/min.
6. Raise crucible and quench with Ar at 1.3 l/min.

7. Further tests will be conducted to determine exact cooling rate.