

Eliminating Crystals in Non-Oxide Optical Fiber Preforms and Optical Fibers

Short Running Title

Gravity and Magnetic Effects on Glass

Author's Names and Affiliations

Dennis S. Tucker

Michael R. LaPointe

NASA

NASA/ZP10

EM20

National Space Science and Technology Center

MSFC, Alabama, USA, 35812

320 Sparkman Drive

Telephone: 256-544-7022

Huntsville, Alabama 35805

FAX: 256-961-9604

Telephone: 256-961-7555

dr.dennis.tucker@nasa.gov

michael.r.lapointe@nasa.gov

Abstract

Non-oxide fiber optics such as heavy metal fluoride and chalcogenide glasses are extensively used in infrared transmitting applications such as communication systems, chemical sensors, and laser fiber guides for cutting, welding and medical surgery. The addition of rare earths such as erbium, enable these materials to be used as fiber laser and amplifiers. Some of these glasses however are very susceptible to crystallization. Even small crystals can lead to light scatter and a high attenuation coefficient, limiting their usefulness. Previously two research teams found that microgravity suppressed crystallization in heavy metal fluoride glasses. Looking for a less expensive method to suppress crystallization, ground based research was performed utilizing an axial magnetic field. The experiments revealed identical results to those obtained via microgravity processing. This research then led to a patented process for eliminating crystals in optical fiber preforms and the resulting optical fibers. In this paper, the microgravity results will be reviewed as well as patents and papers relating to the use of

magnetic fields in various material and glass processing applications. Finally our patent to eliminate crystals in non-oxide glasses utilizing a magnetic field will be detailed.

KEYWORDS

Microgravity, magnetic field, non-oxide glass, crystallization

CONFLICT OF INTEREST

The authors declare no conflict of interest.

1. INTRODUCTION

Heavy metal fluoride glass came to the attention of the scientific and particularly the glass community in 1975. It was at this time that Poulain et al.¹ discovered, quite by accident, a heavy metal fluoride glass while trying to produce a single crystal from the ZrF_4 - BaF_2 - NaF system doped with NdF_3 . These glasses were not very stable, so other metal fluorides were added to aid in vitrification and stabilize the material against crystallization. It was found that addition of a few percent AlF_3 greatly enhanced glass formability.² The addition of NaF to the system enhanced its stability even further.³ The resulting glass system, ZrF_4 - BaF_2 - LaF_3 - AlF_3 - NaF (ZBLAN), is the composition most often used for bulk and fiber optics fabrication. It was soon found that ZBLAN had interesting optical properties, one of which was that it was a very good transmitter in the infrared. It was soon realized that a number of applications could result from this new material. These include fiber amplifiers, fiber optic gyroscopes, lasers for cutting, drilling and surgery, nuclear radiation resistant links, nonlinear optical systems and ultra-long repeaterless, transcontinental and transoceanic links.⁴ However, it was soon realized that producing long lengths of fiber would be problematic.

Intrinsic and extrinsic processes limit light propagation at low powers in ZBLAN.⁵ Intrinsic processes include band gap absorption, Rayleigh scatter and multiphonon absorption. Rayleigh scatter is due to microscopic density and composition fluctuations in the material. UV absorption occurs due to the electronic band edge (Urbach tail) and IR losses occur due to multiphonon absorption. In heavy metal fluoride glasses band gap absorption is negligible in the IR so a theoretical estimate of the minimum loss can be predicted from the intersection of the Rayleigh and multiphonon curves. Theoretical estimates for this loss yields values of approximately 0.001 dB/km for a transmitted wavelength of 2.55 micrometers. The theoretical loss for fused silica is 0.12 dB/km at 1.55 micrometers. Extrinsic processes include impurities such as rare earth and transition metal ions and crystallites formed during preform processing and fiber drawing. These extrinsic processes have a deleterious effect on the real loss value compared to the theoretical value. The presence of OH⁻ has also been observed in bulk and fiber optics.⁶ This ion results in three different absorption bands in ZBLAN glass.^{7,8} Water reacts readily with fluorozirconate melts resulting in HF. Dissolved HF leads to absorption in the glass.⁹ The formation of CO and CO₂, which can contribute to absorption, occur in the presence of oxide and carbon impurities.¹⁰

There are a number of crystals and defects which can serve as scattering centers in ZBLAN glass preforms and fibers.¹⁰ These include ZrF₄, LaF₃, AlF₃, ZrO₂, platinum particles from crucible reactions, carbon from organic impurities and crucible reactions and bubbles due to contraction, cavitation and gas precipitation.¹⁰ Two other crystal phases reported are BaZrF₆ and NaZrF₅ with the former being the most common.^{11,12,13} These crystal phases usually grow on impurities present in the glass. Thus, one goal in production of ZBLAN glass has been to reduce the level of impurities in the starting material and minimize contamination during processing.

Glasses can crystallize either homogeneously or heterogeneously. Homogeneous crystallization is an intrinsic process while heterogeneous crystallization is an extrinsic process. A high rate of homogeneous crystallization indicates poor glass stability. Glass stability is measured in a couple of different ways.¹⁰ The critical cooling rate to avoid crystallization (R_c) is used routinely, however it gives no information on what may occur during reheating for preform fabrication and fiber drawing. The parameter, $(T_x - T_g)$, defined as the difference between the glass transition temperature (T_g) and the crystallization temperature (T_x), is used to describe the thermal stability of a glass during reheating. Both of these techniques are insensitive to small levels (<1%) of crystallinity. If T_g and T_x are close, then crystallization is likely during fiber drawing. Fiber drawing of ZBLAN is not as easy as drawing fibers from oxide glass melts. Oxide glass melts can be drawn into fibers above the liquidus temperature since the viscosity is in the proper range (10^3 - 10^6 poise). The viscosity of ZBLAN above the liquidus is approximately 3×10^{-1} poise which is water like, which means that the viscosity is still low just below the liquidus. Low viscosity means that ionic diffusion will be higher which will lead to rapid crystallization. Thus ZBLAN is normally drawn in a temperature region between T_g and T_x . Since this difference ($T_x - T_g$) is approximately 100C, care must be taken during fiber drawing to avoid crystallization.

2. Fabrication Experiments in Microgravity

Varma et al.^{14,15} studied the effects of gravity on tailored fluorozirconate compositions utilizing statistical design. They stated that devitrification may be due to a narrow working range and low viscosity at the drawing temperature. The first experiments were flown on a T-33 aircraft modified to carry experimental apparatus. This aircraft gives approximately 20 seconds of reduced gravity time by flying a parabola. During the reduced gravity portion of the parabola samples were heated from 325-400C. Unfortunately their results were inconclusive, and they found that in these types of experiments

continuous heating for more than two minutes was necessary to obtain a significant amount of crystallization. In a follow-on study using a sounding rocket to provide approximately 5 minutes of reduced gravity, they found two of eight sample compositions showed no crystallization when heated in reduced gravity. During ground tests, one sample composition ($53\text{ZrF}_4\text{-}20\text{BaF}_3\text{-}4\text{LaF}_3\text{-}3\text{AlF}_3\text{-}20\text{NaF}$) was heated to over 400C in unit gravity for one hour resulting in complete crystallization of the sample. X-ray diffraction analysis of this sample revealed βBaZrF_6 as the major phase, αBaZrF_6 and $\text{Na}_7\text{Zr}_6\text{F}_{10}$ as minor phases with $\text{Ba}_2\text{Al}_4\text{F}_{12}$ in trace amounts.

In later experiments, Anselm and Frischat¹⁶ prepared $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-NaF-InF}_3$ glasses, some of which were doped with metallic silver as a nucleating agent. Three undoped and three doped samples (discs) were flown on an unmanned satellite during a Russian space mission, and while on-orbit were remelted at 800C, held at temperature for 40 minutes, and then cooled to room temperature at a rate of 20K/min below 500C. Unfortunately, five of the samples were destroyed upon retrieval of the satellite, leaving only one doped sample for examination. They found that the glass was very homogeneous away from the crucible walls, which they attributed to the suppression of convective transport processes under weightlessness.

3. NASA ZBLAN Microgravity Experiments

Tucker and Ethridge¹⁷ conducted microgravity experiments to determine the effects of reduced gravity on the crystallization of ZBLAN glass. The first set of experiments utilized NASA's KC135 microgravity aircraft. The second experiment was performed on a sub-orbital rocket.

The first experiment utilized a fiber annealing furnace (FAF) (Figure 1) designed and constructed for use on NASA's KC135 aircraft. The FAF consists of a preheat furnace, annealing furnace and quench block.

The sample was translated manually through each component using a stainless steel push rod. The FAF was mounted in the horizontal position. Two meter lengths of ZBLAN optical fiber were obtained from two different sources.^{18,19} The protective polymer coating was removed chemically, and then the fibers were cut into 25mm lengths. Individual fibers were placed in evacuated quartz ampoules and sealed. Fiber diameters were nominally 300 micrometers. In operation, an individual quartz ampoule is placed at the end of the push rod, and then translated into the preheat furnace for two minutes. This allowed the fiber to reach 250C. Then, during the microgravity portion of the parabola, the ampoule is translated into the annealing furnace for 15 seconds allowing the fiber to reach a temperature of 400C. The crystallization temperature for these fibers was approximately 370C. At the end of 15 seconds the ampoule is translated into a perforated brass quench chamber. Water is used to quench the ampoule via a 60cc plastic syringe. Cooling rates were generally around 40C/sec.

Ground tests were performed to determine the time necessary to reach the nucleation temperature and to run unit gravity studies. A thermocouple was inserted into a glass ampoule and translated into the preheat furnace until the temperature reached 250C and then into the annealing furnace until a temperature of 400C was attained. In this manner, times necessary for preheat and annealing during the parabolic maneuver were established. Five samples of each manufacturer's fiber were then heated at unit gravity to serve as controls.

During the KC135 flights, ten samples of each manufacturer's fiber were heated to 400C during the zero-g portion of the parabola. Actual gravity levels as measured by a three-axis accelerometer during the 20-25 second period of the zero-g portion of the parabola were in the 0.01 to 0.001 g level.

The processed samples were examined with optical and scanning electron microscopy. X-ray diffraction was performed to determine the crystal phases.

In order to determine if longer soak times at the crystallization temperature would increase the likelihood of crystallization, fiber samples were flown on a Starfire 1 suborbital rocket provided by EER Systems. The suborbital rocket provided 6.6 minutes of microgravity. The fibers were the same type used in the KC135 experiments, except that one group were 300 micrometers in diameter, while the other group were 530 micrometers in diameter. Sample preparation was identical to that of the KC135 experiments.

A fiber processing furnace (Figure 2) was designed and constructed as a payload on the Starfire I sounding rocket flight launch on April 3, 1996 at White Sands Missile Range, New Mexico. Analysis consisted of optical and scanning electron microscopy and x-ray diffraction.

4. Experiment Results

From an operational standpoint the experiment worked as planned during the flight. However, it was learned that after recovery of the rocket payload that nine of the twelve sample ampoules had cracked and the ZBLAN fibers were immersed in the water saturated sponges. Failure of the ampoules occurred after the samples had been retracted into the quench assembly and was probably due to impact of the payload with the ground. This led to water catalyzed crystallization of the samples. The three samples which survived were ones that had been heated to the pulling temperature of 323C for the two of the fibers and 340C for the other. None of these showed evidence of crystallization. Samples heated to the same temperature on the ground showed evidence of crystallization.

An electron micrograph of a fiber processed at 400C in microgravity is shown in Figure 3. Figure 4 shows a fiber processed at 400C in unit gravity. The fiber in Figure 4 shows obvious signs of crystallization. This was true for all the fibers processed in unit gravity. No signs of crystallization were seen in the microgravity processed fibers.

5. Effects of Magnetic Fields

Magnetic fields have been used successfully to affect flows in conducting fluids. Crystals grown from melts are improved by using uniform^{20,21,22,23} and rotating magnetic fields.²⁴ Convective heat and mass transport in semiconductor melts with large electrical conductivities can be controlled by magnetic fields. The effects of DC and AC fields are different; a DC field tends to produce a body force which opposes or damps the buoyant convection, while AC fields drive melt motions.²⁵ The effects of magnetic fields on g-jitter driven flow under microgravity have been investigated,²⁶ as well as magnetic field effects on the crystallization of inorganic salts. The reported results vary for magnetic field effects on inorganic salt crystallization; it has been found that calcium carbonate crystallization decreases under a magnetic field,²⁷ while soluble diamagnetic salts of weak acids were shown to have accelerated crystallization.^{28,29} In addition, Wang et al.³⁰ were able to retard crystallization in a bulk amorphous alloy using a high (10-T) magnetic field.

6. Magnetic Field Experiment

A solenoid electromagnet with a magnetic field strength of 0.1-T was used for this investigation. The magnetic field direction could be reversed by changing the polarity on the power supply. A furnace capable of 400°C was constructed to hold the ZBLAN glass optical fibers. The furnace was mounted in the center of the electromagnet, providing accurate fiber alignment with the solenoid axis. The axial magnetic field was uniform (+/- 2%) over the full length of the ZBLAN fiber sample. A photograph of the test system is shown in Figure 5.

Nine ZBLAN fibers were used in this study. The fibers were 50mm in length and 300 micrometers in diameter. A polymer buffer coating was chemically stripped. All fibers were encapsulated in fused quartz ampoules, and backfilled with helium to protect the samples from water contamination and to aid in heat transfer. Three samples were heated to the crystallization temperature (345°C) for 45 seconds with

the magnetic field vector parallel to the gravity vector, and three samples were heated in the same manner with the magnetic field vector anti-parallel to the gravity vector. The final three samples were used as controls, and were heated in the same manner but without a magnetic field. The heating time was limited by the resistance heating of the un-cooled electromagnetic coils. After processing the samples were observed with a stereo-optical microscope and a scanning electron microscope (SEM). X-ray diffraction was used to identify the crystal type.

7. Magnetic Field Results

When viewed under optical microscopy, the three control samples exhibited “frosting” representative of crystallization. Detailed crystal structures were viewed using scanning electron microscopy (Figure 6). The crystal structure was identified as BaZrF_6 , the most common crystal type for ZBLAN. The fibers heated in the 0.1-T magnetic field did not show evidence of crystallization under optical microscopy or SEM. Figure 7 shows a representative fiber sample heated in the magnetic field with the magnetic field vector anti-parallel to the gravity vector. Figure 8 is an example of a fiber heated with the magnetic field vector parallel to the gravity vector. While there are minor irregularities in the surface of the fiber, the crystallization apparent in the control samples was not observed.

It was initially hypothesized that the mechanism for suppression of crystallization was the permeability difference between the amorphous glass and the crystallites. Assuming the formation of spherical nuclei in solids, the change in free energy without a magnetic field consists of three parts: bulk free energy, strain energy and surface energy³⁰

$$\Delta G = \frac{4}{3}\pi r^3(\Delta G_v + \varepsilon) + 4\pi r^2\sigma \quad (1)$$

where r is the radius of the nucleus, ΔG_v and ε is the bulk free energy decrease and strain energy increase per unit volume, respectively, and σ is the interfacial energy increase per unit area of interface between a nucleus and matrix. The strain energy is usually negligible since the supercooled phase can relax any misfit induced strains.

When a magnetic field is applied to a material, the work induced by the magnetic field can be expressed as³⁰

$$G = \frac{1}{2} \int_v BH dv = \frac{1}{2} \int_v \mu H^2 dv = \frac{1}{2} \mu H^2 \frac{4}{3} \pi r^3 \quad (2)$$

where, μ is the magnetic permeability and H is the intensity of the applied magnetic field. As phase transformations occur, new phases precipitate from the matrix and the permeability of the sample changes from μ_1 to μ_2 . Therefore, the contribution to phase transformation by the free energy change under a magnetic field is

$$\Delta G_M = \frac{1}{2} H^2 (\mu_2 - \mu_1) \frac{4}{3} \pi r^3 \quad (3)$$

Here μ_1 is the permeability of the parent phase (glass) and μ_2 is the permeability of the new crystalline phase. In all, the total free energy change of a material under a magnetic field is given by

$$\Delta G = \frac{4}{3}\pi r^3[\Delta G_v - \frac{1}{2}H^2(\mu_2 - \mu_1)] + 4\pi r^2\sigma \quad (4)$$

Then, the free energy required for the formation of a critical nucleus (ΔG_c) obtained by setting $d\Delta G/dr = 0$ is

$$\Delta G_c = \frac{16\pi\sigma^3}{3[\langle\Delta G_v\rangle + \frac{1}{2}H^2(\mu_2 - \mu_1)]^2} \quad (5)$$

where $\langle G_v \rangle$ is defined as the absolute value of the volume free energy.

From equation (5), it can be seen that the effect of a magnetic field yields two measurable variables: the intensity of the applied magnetic field, and the permeability difference.

To test the hypothesis that permeability may play a role in suppressing crystallization, the magnetic susceptibility of ZBLAN glass and crystallized ZBLAN were measured. A 4mm thick by 11mm diameter sample of glass was crystallized fully by heating to 345°C for 6 hours.

The magnetic susceptibility of the samples was measured using a vibrating sample magnetometer (Digital Measurement System Model 880 VSM) with maximum applied field strength of 13 kOe. The VSM

is calibrated using a Ni standard sample with 6.35mm diameter and 50 micrometers thickness, which has a saturation magnetic moment of 0.718 ± 0.011 emu at 20⁰C. The background moment from a quartz sample holder and substrate was also measured and automatically subtracted during measurement. The dimensionless volume magnetic susceptibility, represented by the symbol, χ_v , is defined by

$$M = \chi_v H \quad (6)$$

where M is the magnetization of the material (magnetic dipole moment per unit volume) measured in emu, and H is the applied magnetic field, measured in Oe. Thus, the magnetic susceptibility is defined by the ratio of M / H . The susceptibilities were converted to S.I. units and the permeability was calculated using

$$\mu = \mu_0(1 + \chi_v) \quad (7)$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$ is the permeability of free space.

The calculated permeabilities were $\mu_1 = 12.559857$ microH/m and $\mu_2 = 12.559842$ microH/m. There is no significant numerical difference in these values, which eliminates a difference in permeability

between glass and crystal as being the mechanism of suppressed crystal growth. A whole number change in the permeabilities would be necessary to the change in free energy enough to warrant this as a mechanism for crystal suppression.

It is evident from the results that both microgravity and an axial magnetic field have the effect of suppressing crystallization in ZBLAN. Whether there is one mechanism common to both, or if two different mechanisms are in effect is unknown at this time. The possibility that the magnetic field increases the viscosity of the glass and reduces the viscous flow velocity, similar to what would occur in reduced gravity, remains under investigation. Nevertheless, based on the ground based experiments, it was determined that a process could be developed utilizing an axial magnetic field to suppress crystallization in non-oxide glasses.

The above results are qualitative in nature, i.e. crystals are present or not in the processed samples. A quantitative approach would involve a nucleation and growth study. This has been proposed as a part of a mechanism study utilizing our superconducting magnet. Measurement of viscosity in a magnetic field would also be compared to that out of the magnetic field. This would test the hypothesis that an increase in viscosity in a magnetic field suppresses nucleation and growth via suppression of convective flow. As part of this study, preforms of ZBLAN will be processed as described below in the discussion of eliminating crystals in preforms. These preforms will then be drawn into fibers and the attenuation coefficients measured and compared to fibers drawn from as-received preforms.

This approach could also be applied utilizing microgravity. A mechanism study would however, require processing for long periods. The only platform available at this time is the International Space Station. Funding for this type of study will be sought in the future.

One of the authors (Tucker) is involved in a Department of Defense study in which it will be attempted to draw continuous fibers from ZBLAN preforms on board a sub-orbital rocket. This experiment is

planned for 2013. The attenuation coefficient of the drawn fiber will be compared to that of drawn in unit gravity.

8. Patent Review

The following patents discuss various methodologies for producing optical fiber preforms and optical fibers with improved transmission properties.

Bocko et. al.³¹ discuss an improved method for making sodium-containing glasses via a vapor deposition process. The sodium is useful as a modifier to control optical, melting and forming processes in halide glasses.

Nice³² invented a double crucible fiberizing apparatus and processes for forming core/clad fluoride glass fibers well below the liquidus temperature of the fluoride glasses. This invention relates to the rapid fiberization of fluoride glasses in order to yield non-hollow, crystal field fibers. The double crucible is located within an environmentally controlled chamber. The double crucible comprises an inner crucible located within an outer crucible. The outer crucible is heated by passing an electric current through it. Low pressures applied to the crucible (less than 10 psi) are adequate to produce 55 meters/minute drawing speeds.

Mollenauer et. al.³³ produced doped optical fiber preforms by inserting a doped filament into a substantially completed preform such that the filament would be centrally located in the core region upon collapse or consolidation of the preform. Thus the dopant concentration level was controllable and calibrated to achieve the desired concentration in the resulting fiber.

Ishikawa et. al.³⁴ provide a process for thermal treatment for the stable production of an optical fiber preform from which preform an optical fiber can be drawn. This consists of dehydrating and purifying a porous glass preform via heating in a muffle furnace having a SiC layer on the inner surface of the muffle tube under an atmosphere comprising an inert gas and a silicon halogen gas. It also provides a process for fluorine-doping treatment of the porous glass preform.

Berkey et. al.³⁵ present an invention providing a method of forming a glass article such as a waveguide preform, substantially free of inclusions such as gas bubbles and crystallites. The method comprises the steps of providing an elongated, consolidated glass preform having a longitudinal aperture and drawing the preform in two steps to provide a rod. The first step consists of heating at least one end of the preform rod and drawing the preform to provide a reduced diameter preform. The second step involves heating at least one end of the preform and further drawing to reduce the diameter of the preform. This method also includes closing one end of the aperture and evacuating the aperture.

In order to address the problem of devitrification in chalcogenide glasses, Hewak et al.³⁶ provide a new and improved hybrid of Ga:La:S glass. This hybrid is in the Ga:La:S group, comprising Ga, La, S, O, and F with at least 2 mol% lanthanum fluoride. This hybrid has thermal properties highly suitable for fiber drawing. This hybrid is incorporated into an optical waveguide, with a clad glass of Ga:La:S and core glass of Ga:La:S:O:F glass.

Petisce³⁷ utilized a magnetic field during fiber drawing of silica optical fibers. He stated that the magnetic field aligned electron spins of the free radicals on the fiber surface thereby healing surface defects. He stated that a magnetic field of at least 2 kilogauss was necessary for this process to be effective.

Kopylov et al.³⁸ invented a method of eliminating bubble formations and crystallites in optical fiber preforms to produce low loss optical fibers. This invention utilizes glasses that have low viscosity in their

liquid state (i.e. heavy-metal fluoride glasses). In one embodiment of this method a molten fluoride glass is simultaneously vacuum-pumped and slow-cooled from the liquidus temperature to the casting temperature, and then poured into a cylindrical casting mold. It is then cooled such that a temperature gradient forms across the axial length of the cooling glass and such that the cooling glass solidifies from its outside perimeter to its cylindrical axis with no crystallization or bubble formation.

Aggarwal et al.³⁹ invented a method of reducing bubbles and associated crystallites by using hot isostatic pressing slightly below the softening point. External pressure is applied via a mechanical die and a smooth, nonadherent surface or gas pressure, on the material surface to enhance densification, producing a fully dense structure. Bubbles formed during glass processing are thereby removed at temperatures below which crystallization of the glass occurs, facilitating the production of geometrically undistorted glass structures in which transmission losses due to extrinsic scattering are reduced or eliminated.

9. Eliminating Crystals in Non-Oxide Optical Fiber Preforms and Optical Fibers

Based upon research by Tucker et al.⁴⁰ it was decided to apply the results to developing a process to eliminate crystals in non-oxide preforms such as heavy metal fluoride and certain chalcogenide glasses. This method consists of the following⁴¹: 1) Heating a non-oxide optical fiber preform to a temperature sufficient to melt any crystallites present in the presence of a vertically aligned magnetic field. The preforms long axis is aligned axially along a vertical magnetic field. 2) Once the preform is at the prescribed temperature to melt any crystallites, the preform is kept at this temperature for at least 20 minutes to allow the crystallites to melt. 3) The preform is then cooled rapidly to the glass transition temperature in order to avoid crystallization while still within the vertical magnetic field. 4) The preform is held at the glass transition temperature for 20 minutes in order to anneal out any thermal stresses

present from the rapid cool down. 5) The preform is then allowed to cool to room temperature. See figure 9.

Our experiments indicate that the combination of a vertical magnetic field and a rapid cool down from the crystallite melting temperature will ensure that no crystals are present in the preform after processing.

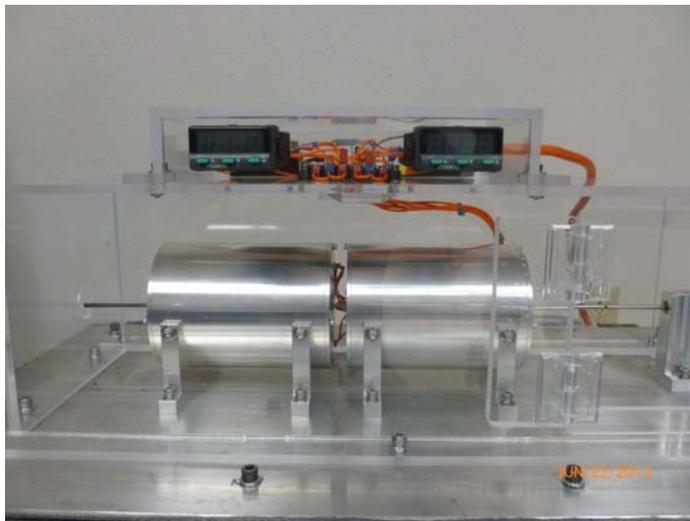


Figure 1 – Fiber Annealing Furnace

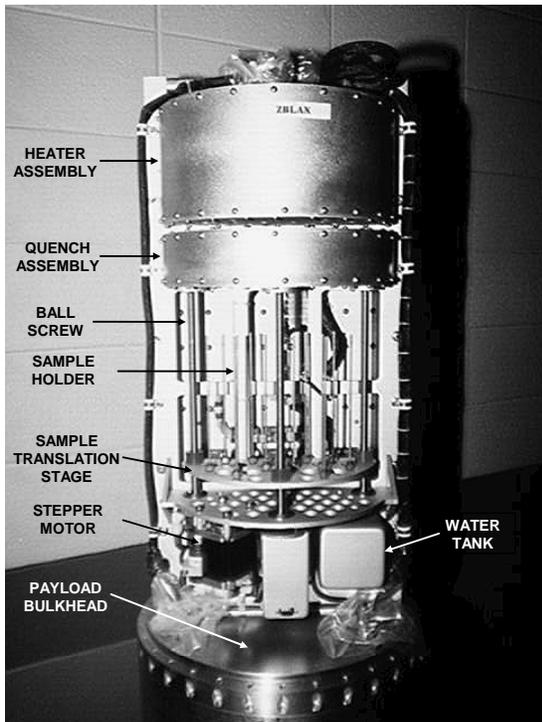


Figure 2 Conquest Rocket Payload

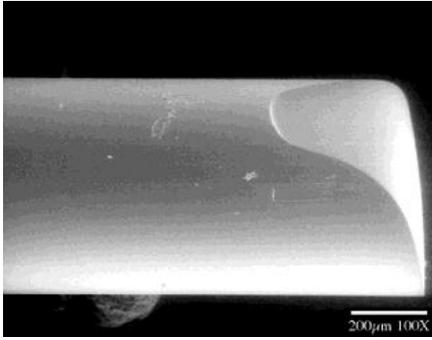


Figure 3 ZBLAN Fiber Processed in Microgravity

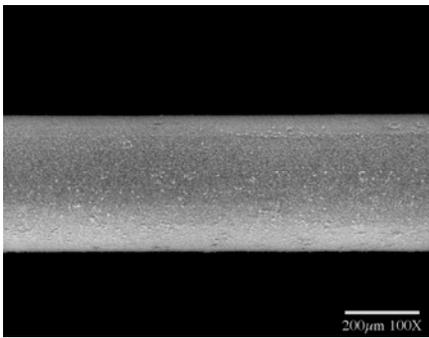


Figure 4 ZBLAN Fiber Processed in Unit Gravity



Figure 5 Axial Magnet Test Set-up



Figure 6 ZBLAN Fiber Heated In Unit Gravity

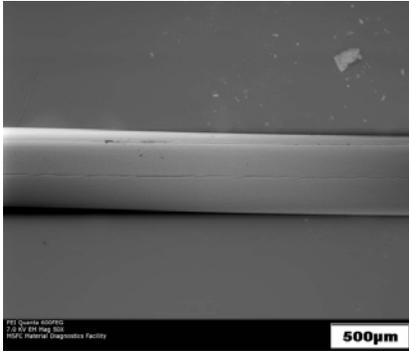


Figure 7 ZBLAN Fiber with Magnetic Vector Parallel to Gravity Vector

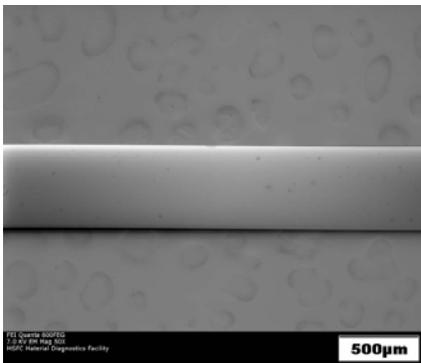


Figure 8 ZBLAN Fiber with Magnetic Vector Anti-parallel to Gravity Vector

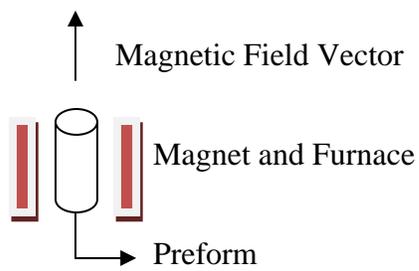


Figure 9 Concept for Eliminating Crystals in Non-Oxide Preforms

References

1. Poulain, M. Poulain, M., Lucas, J. and Brun, P. Mat. Res. Bull., Verres Fluores au Tetrafluore de Zirconium Proprieties Optiques d'un Verre Dope au Nd³⁺, 1975, 10, 243-246.
2. Lecoq, A. and Poulain, M. J. Non-Cryst. Solids, Fluoride Glasses in ZrF₄-BaF₂-YF₃-AlF₃ Quaternary System, 1980 41, 209-213.
3. Mitachi, S., Terunuma, Y. Ohishi, Y. and Takahashi, S., Reduction of Impurities in Fluoride Glass Optical Fibers, Jpn. J. Appl. Phys., 1983, 22, L537-L538.
4. Tran, D.C., Siegel, G.H., and Bendow, B., J. Lightwave Technol. Heavy Metal Fluoride Glasses-A Review, 1984, LT-2 (5), 566-586.
5. Bansal, N.P., Bruce, A.J., Doremus, R.H. and Moynihan, C.T., Crystallization of Fluorozirconate Glasses, 1984, Mat. Res. Bull., 19, 577-590.
6. France, P.W., Carter, S.F., Williams, J.R., Beales, K.J., and Parker, J.M., OH Absorption in Fluoride Glass Infrared Fibers, 1984, Electron. Lett., 20, 607-608.
7. Fjeldly, T.A., Hordvik, A. and Drexhage, M.G., Stability of IR Transparent Fluoride Glasses in Humid Air Studied by Auger Electron Spectroscopy, 1984, Mat. Res. Bull., 19, 685-691.
8. Mitachi, S. and Miyashita, Y., Preparation of Low-Loss Fluoride Fibers, 1982 Electron. Lett., 18, 170-171.
9. Buswell, A.M., Maycock, R.L., and Rhodebush, W.H., Infrared Absorption Studies X: The IR Absorption of HF in the Vapor State and in Solution in an Inert Solvent, 1940, J. Chem. Phys., 8, 362-368.
10. Sanghera, J.S., Busse, L.E., Aggarwal, I.D., and Rapp, C., (1998), Fluoride Glass-Based Fibers, in J.S. Sanghera and I.D. Aggarwal (Eds.), *Infrared Fiber Optics*, (1st edition, pp. 75-142), Boca Raton, Florida: CRC Press.
11. Drehman, A.J., Crystallite Formation in Fluoride Glasses, 1987, Mat. Sci. Forum, 19-20, 2, 483-489.
12. Parker, J.M., Seddon, A.B., and Clare, A.G., Crystallization of ZrF₄-BaF₂-NaF-AlF₃-LaF₃ Glasses, 1987, Phys. Chem. Glasses, 28, 1, 4-10.
13. deLeede, G., deWaat, H., and Hakkens, F., Nucleation in ZBLAN Glasses, 1989, J. Amer. Cer. Soc., 72, 10, 1991-1992.
14. Varma, S., Prasad, S.E., Murley, I., Wheat, T.A. and Abe, K., The Role of Statistical Design in Microgravity Materials Research., 1991, Proceedings Spacebound 91, 248-249.
15. Varma, S., Prasad, S.E., Murley, I., Wheat, T.A. and Abe, K., Microgravity Processing of Fluorozirconate Glasses Aboard CSAR-1: Preliminary Results, 1992, Proceedings of Spacebound 92, 109-114.

16. Anselm, L., and Frischat, G.H., Early Crystallization Stages in a Heavy Metal Fluoride Glass Prepared under Normal and Weightless Conditions, 2000, *Phys. Chem. Glasses*, **41**, 32-37.
17. Tucker, D.S. and Ethridge, E.C., "Explanation of the Effects of Gravity on Crystallization of ZrF₂-BaF₂-LaF₃-AlF₃-NaF Glass", *J. Mater. Res.*, Vol. 16, No. 11, 2007.
18. D.C. Tran, Infrared Fibers Systems Inc., Silver Springs, MD 20904.
19. T. Truex, Galileo Electro-Optical Corp., Sturbridge, MA
20. D.T.J. Hurle, *Handbook of Crystal Growth*, North-Holland, Amsterdam, 1994.
21. V. Galindo, G.Gerbeth, W. von Ammon, E. Tomzig and J. Virbulis, *Energy Convers. Manage.*, **43**, 309, 2002.
22. A.I. Fedoseyev, E.J. Kansa, C. Marin, A.G. Ostrogorsky, *Proceedings of the 8th ISCFD*, ZARM Bremen, 1999.
23. P.J. Prescott and F.P. Incropera, *Trans. ASME*, **115**, 202, 1993
24. O. Patzold, I. Grants, U. Wunderwald, K. Jenker, A. Croll and G. Gerbeth, *J. Cryst. Growth*, **245**, 237, 2002.
25. J.S. Walker, *Progress in Crystal Growth and Characterization*, 195, 1999.
26. B. Pan, D-Y Shang, B.Q. Li and H.C. de Groh, *Intern. J. of Heat and Mass Transfer*, **45**, 125, 2002.
27. H. E. Lundager Madsen, *J. of Cryst. Growth*, **267**, 251, 2004.
28. A.M.B. Freitas, F.J.G. Landgraf, J. Nyvlt and M. Giuliatti, *Cryst. Res. Technol.*, **34**, 1239, 1999.
29. H.E. Lundager Madsen, *J. of Cryst. Growth*, **152**, 94, 1995.
30. S. Berg, R. Kroger and H.J. Rath, "Measurement of Extensional Viscosity by Stretching Large Liquid Bridges in Microgravity", *J. Non-Newtonian Fluid Mech.*, **55**, 307, 1994
31. X. Wang, M. Qi and S. Yi, *Scripta Mat.*, **51**, 1047, 2004.
32. Bocko, P.L., Thompson, D.A., and Wein, W.J., *Methods for Making Sodium-Containing Glass*, US Patent number 4,645,524, 1987.
33. Nice, M.L., "Apparatus and Process for Fiberizing Fluoride Glasses using a Double Crucible and the Compositions Thereby", US Patent number 4,897,100, 1990.
34. Mollenauer, L.F., Simpson, J.R., and Walker, K.L., "Fabrication of Doped Filament Optical Fibers", US Patent number 5,059,230, 1991.
35. Ishikawa, S., Ohga, Y., Tsuchiya, I., Kanamori, H., Yokota, H., and Kyoto, M., "Process for Thermal Treatment of Glass Fiber Preforms", US Patent number 5,306,322, 1994.
36. Berkey, G.E., Chu, P.W., Crossland, C.E., Moore, L.A., Qi, G., and Solosky, J.W., "Method of Making a Glass Preform", US Patent number 6,418,757, 2002.

37. Hewak, D.W. and Mairaj, M.K.A., "Optical Waveguides and Optical Fiber Preform including Gallium, Lanthanum, Sulfur, Oxygen and Fluorine", US Patent number 7,016,593, 2006.
38. Petisce, J.R., "Methods and Apparatus for Increasing Optical Fiber Draw Speed", US Patent number 5,314,519, 1994.
39. Kopylov, N. and Kortan, A.R., "Method of Eliminating Light Scattering Bubbles in Optical Fiber Preforms", US Patent number 5,776,222, 1998.
40. Aggarwal, I.D. and Harbison, B.B., "Hot Isostatic Pressing of Fluoride Glass Materials", US Patent number 5,078,768, 1992.
41. Tucker, D.S., LaPointe, M.R., and Jia, Z., "The Effects of a Magnetic Field on the Crystallization of a Fluorozirconate Glass", J. Mat. Res., vol. 22, no. 6, 2007.
42. Tucker, D.S. and LaPointe, M.R., "Eliminating Crystals in Non-Oxide Optical Fiber Preforms and Optical Fibers", US Patent 7,848,606 B1, 2010.