

Final Report: Optical Properties of ZBLAN Microspheres Produced in Microgravity

April 11, 2002

Serena Eley, Dirk Englund, John Ferguson, Joseph Jewell, Daniel Stick,
Nathan Wozny
*California Institute of Technology, 1200 East California Boulevard,
Pasadena, California 91125*

Advisers: Lute Maleki, Vladimir Ilchenko
*Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California
91109*

Abstract

Microspheres of doped and undoped ZBLAN were fabricated in microgravity. Their optical properties were to be compared with microspheres fabricated in a 1g environment. Silica-based fibers were produced as a control.

The optical transmission properties of ZBLAN can be deduced from the longevity of whispering gallery modes induced in microspheres of the glass. Fabricating spheres promises a much simplified means of measuring the attenuation of ZBLAN since no fiber needs to be pulled in 0g.

This first trial of the experiment was troubled by surface contamination and material breakdown. The resulting microspheres were too poor in quality to be used as light resonators.

A follow-up experiment will improve these issues. It employs a new heating method and improved contamination prevention measures.

1 Introduction

Heavy metal fluoride glasses (HMFGs) show great promise as fiber optic materials. With the possibility of far lower attenuation rates than current

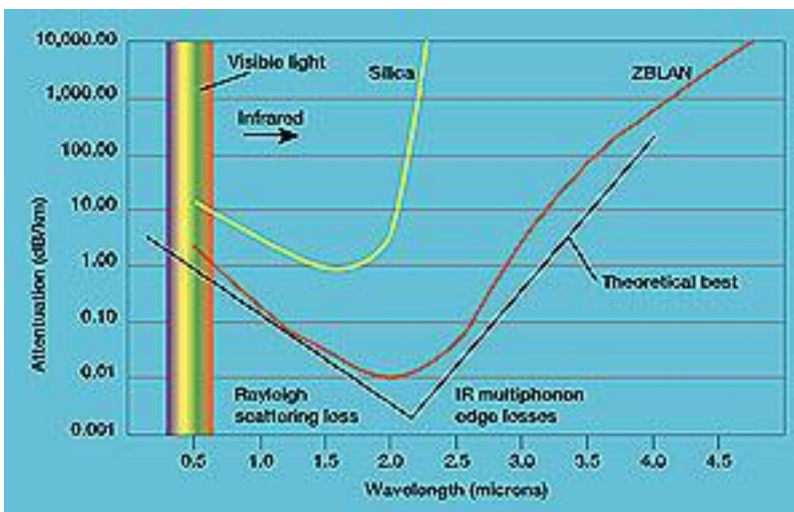


Figure 1: ZBLAN’s attenuation approaches the theoretical minimum allowed by matter.

silica-based materials (as low as 0.001 dB/km, cf. 0.2 dB/km for Si-based fibers), the most promising of the heavy metal fluoride glasses is $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$ (ZBLAN). Theoretically, ZBLAN fibers could carry light with an attenuation near the theoretical best allowed by matter [6], see 1. In addition to its low attenuation, ZBLAN provides a larger spectral window. This property is especially important for increased bandwidth in data transmission applications [7].

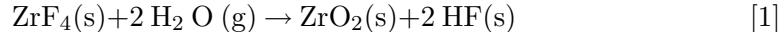
Given these advantages, why isn’t ZBLAN used commercially? The reason is that amorphous ZBLAN is very difficult to produce. When fabricated in a gravity environment, tiny crystals form that destroy the material’s transmittance properties. In microgravity, this crystallization is sharply reduced [8]. Recent microgravity experiments give vital clues as to how this gravity-induced crystallization process takes place, so that ways may be found to avoid it on the ground.

Even if produced in microgravity, ZBLAN will crystallize if it is not cooled rapidly enough. To achieve fast cooling requires that the sample be made with a high surface area to volume ratio. In addition, the sample’s geometry must allow for easy light attenuation measurements.

Microspheres offer a good solution to both of these issues. Because they are only about 200 μm in diameter, they equilibrate very quickly with their surroundings, so that very fast temperature changes are possible. They also

present a very convenient, accurate way of measuring attenuation: whispering gallery modes (WGM), induced around the perimeter of the sphere, decay in accord with the material's attenuation coefficient. The intensity thus behaves much like the energy of a damped harmonic oscillator. The quality factor Q of the microsphere resonator thus measures the damping term, i.e., the attenuation of the ZBLAN material. Therefore, knowledge of the effects of gravity on Q could be used to infer the crystallization process during the solidifying stage of ZBLAN.

To compare absorption based on measurements of Q , one needs to reduce the other factors affecting Q . Research on silica-based microsphere resonators has shown that two other appreciable factors are the loss due to surface scattering and the loss due to optical absorption by water in the surface of the sphere [4]. Water absorption has a far more deteriorating effect in ZBLAN than in Si-based spheres [5]. The following reaction occurs:



Surface scattering in microspheres losses depend largely on two factors: surface inhomogeneities, which cause diffusive scattering, and surface curvature, which causes a greater fraction of light to be refracted to the outside of the sphere. Thus, surface scattering can be reduced by cleaning the surface and/or increasing the sphere's radius.

In fabricating the microspheres in $0 \cdot g$, the flyers made an effort to make them as large as possible. The average diameter was about $200 \mu\text{m}$ for undoped ZBLAN microspheres, about $100 \mu\text{m}$ for doped ZBLAN microspheres, and about $250 \mu\text{m}$ for silica-based spheres.

In addition to the higher Q values, there is reason to believe that erbium-doped ZBLAN microspheres can be used to create improved low threshold green lasers. These resonators have a range of technological and scientific applications, i.e. in future optical communication devices, interferometric sensing, high resolution spectroscopy, data storage, lasers, and in combination with many other photonic devices. [1]

If the experiment had not been plagued by water contamination, we predicted that the ZBLAN spheres produced in microgravity would have higher Q -factors than those produced on the ground. On the other hand, the silica-based spheres would have shown no significant difference in the Q -factor.

Twenty ZBLAN and ten silica microspheres were produced in microgravity. Of the ZBLAN spheres, roughly half were Er-doped; the others were undoped. Because of overheating and contamination, none of the ZBLAN

spheres were usable as resonators. Therefore, nothing could be concluded about the difference in light attenuation between $0 \cdot g$ and $1 \cdot g$ ZBLAN samples. The Si-based microspheres produced with and without gravity had agreeing Q -values, confirming the assumption that gravity-aided crystallization plays no significant role in the solidification process of Si-based glass.

Despite its limited success, this experiment was extremely instructive for designing a follow-up experiment. In the follow-up experiment, heating coils will be used to melt the ZBLAN fibers. This method will allow for far greater control than the inhomogeneous and excessively hot plasma heating method used previously. Several improvements will be made to prevent water contamination. Furthermore, the experiment will be largely automated to make human error during flight less likely.

2 Experimental

The experiment consists of four major components: preparing fibers, forming microspheres in $0 \cdot g$ and $1 \cdot g$, measuring the light attenuation factors, and determining material properties, e.g. crystallization frequency.

2.1 Preparing Fibers

The first requirement for good microspheres is starting with pure samples. For our project, this primarily meant keeping water contamination (from the air or from etchants) to a minimum.

We custom ordered samples of ZBLAN fibers. These fibers were cladded only with a protective layer of acrylate. Removing this cladding at the sites where the spheres would be formed is rather difficult. For etching the cladding, we chose dichloromethane as it appeared to introduce the least amount of water contamination. We exposed the fibers to dichloromethane vapor for 5 minutes. This is enough time to loosen the acrylate coating without significantly attacking the ZBLAN (if ZBLAN is exposed much longer, it tends to become much more brittle). Then we stripped the loose coating off with needle-nose pliers.

After the fibers were produced, they were stored in a vacuum container where they remained until just before the flight on the KC-135. The vacuum containers were pumped to 10^{-2} Torr using a rough pump and a turbo pump. By keeping the samples in this very low concentration of water, water molecules in the sample surface are evaporated off the sample.

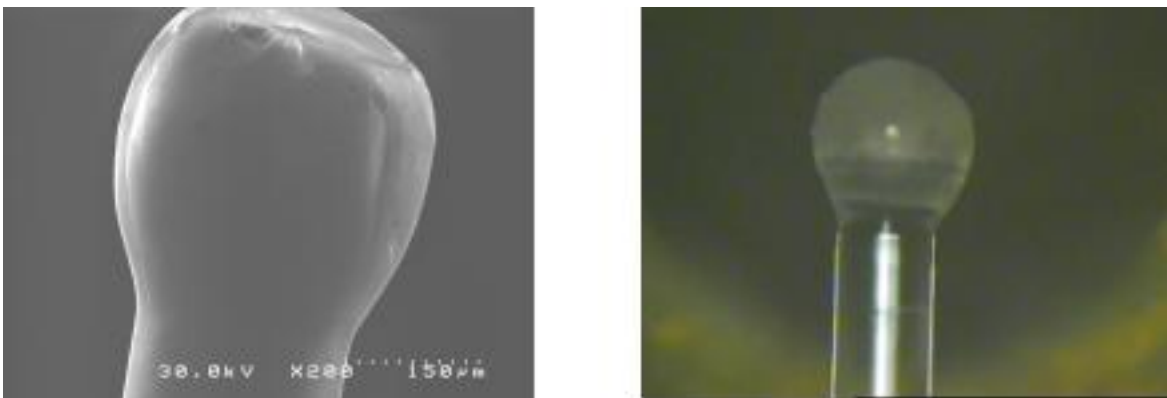


Figure 2: A ZBLAN microsphere produced in microgravity using FW-304 fiber splicer. Left: SEM.

2.2 Fabricating Microspheres

The fabrication process requires bringing the glass to its melting point and then allowing it to cool. While the glass is liquid, surface tension causes it to pearl up into a spherical shape. To heat the sample, we chose to use a fiber splicer, a device that applies a high voltage (30 kV) RF between two closely spaced electrodes. If the voltage is high enough, the air breaks down, creating a plasma hot enough to melt ZBLAN and silica-based fibers.

The experiment showed that the fiber splicer overheated the ZBLAN samples. This resulted in rather misshapen spheres, see Fig. 2.

2.3 Measuring Q

To determine Q , we measured resonant light intensity inside the microsphere as a function of the frequency of the input laser. From FWHM ($= \Delta f$) of the resulting resonance curve, we could calculate $Q = \frac{f_0}{\Delta f}$, where f_0 is the resonance frequency. The attenuation coefficient is related to Q by $\beta = \frac{2\pi f}{Q}$.

To excite the microsphere resonator and measure the intensity inside, we need to couple the input and output fibers to the sphere. We did this using tapering and prism methods. In the tapering method, a signal is sent through a tapered single-mode fiber. Around the tapered part, the effervescent field is strong enough to excite whispering gallery modes inside the adjacent sphere. The intensity of the resonance modes is measured by the same fiber. From the intensity vs. laser frequency plot, the FWHM and thus the Q of the resonator is determined (see 3). See Figures 4 for the

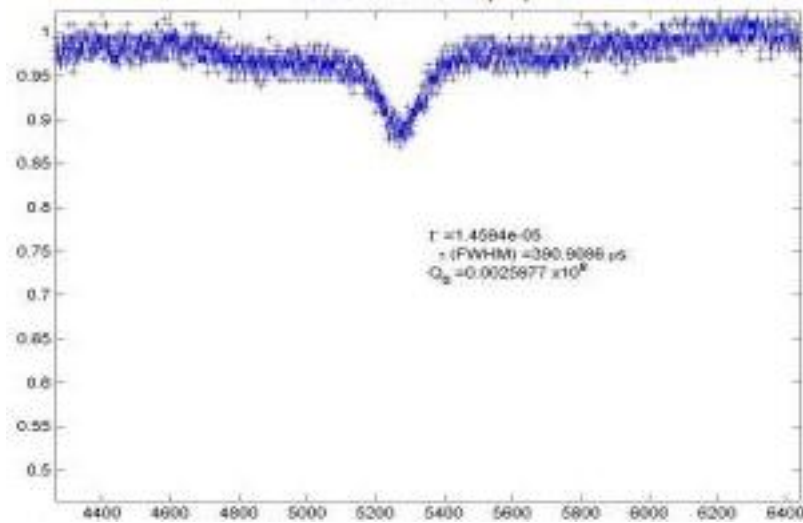


Figure 3: Resonance curve obtained for Si-based sphere at $\lambda = 555\text{nm}$. The tapering method was used to couple light into the microsphere and measure the response.

tapering method that Dr. Vahala let us use in his Caltech lab.

The tapering method used at JPL differed slightly, see Fig. 5. In this setup, the beam from a tunable laser is coupled to the microsphere using a prism. The laser frequency is swept across resonance. The output of the beam, proportional to the light intensity inside the resonator, is displayed on an oscilloscope. A Fabry-Perot cavity of known length, which is being swept at the same time, serves to calibrate the sweep time with the corresponding laser frequency.

The prism method is required for ZBLAN spheres to match the index of refraction of the coupling optics with the index of refraction of ZBLAN. A dielectric surface of higher refractive index is positioned close to the sphere. Radiation is coupled into such a mode by optical tunneling through the gap between the microsphere and a prism [2]. Fig. 6 depicts a ZBLAN microsphere being characterized using this method.

2.4 Evaluating Material Properties

The Q -values and resonance curves of ZBLAN or silica-based fibers can only hint at material properties.

To probe deeper, we took scanning electron microscope images of the

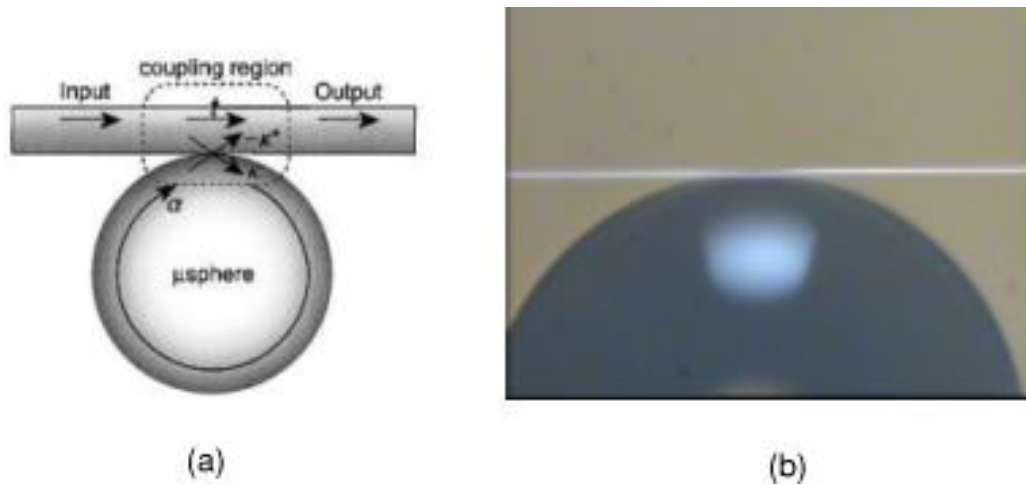


Figure 4: Tapering method used at Caltech: (a) Schematic of tapering technique, as used by [3]; (b) One of the silica-based microspheres produced in microgravity is being characterized using the tapering technique.

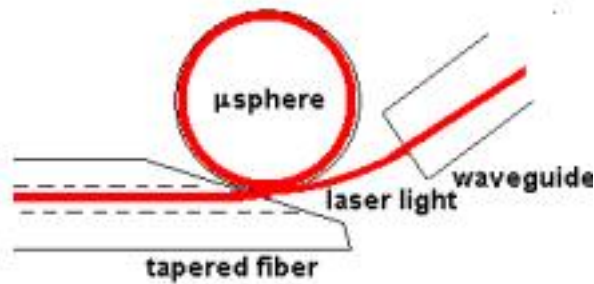


Figure 5: Tapering method used at JPL.

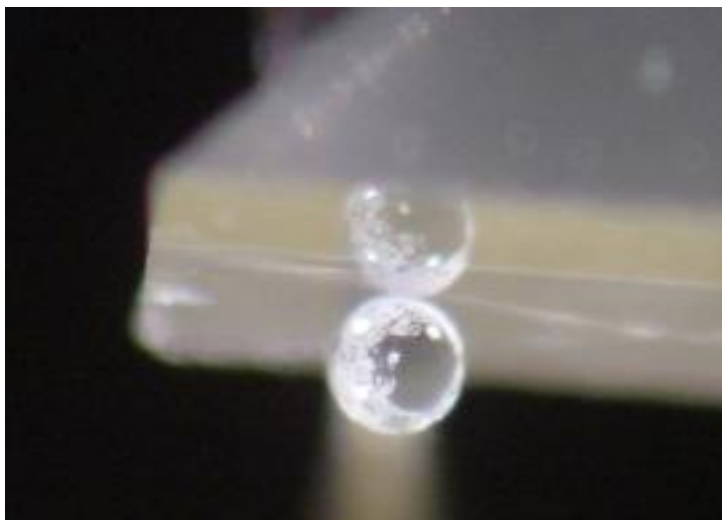


Figure 6: (a) Characterization of ZBLAN microsphere using prism method [3].

samples. We were looking for two important factors that deteriorate the quality of the resonator: crystallization and surface irregularities. The SEM image in Fig. 7 shows clear signs of surface irregularities on the ZBLAN sphere. The surface had been heated to a temperature between 500 and about 900 °C, much higher than the melting temperature of ZBLAN (265 °). As a result, the surface is visibly scorched.

To look for crystallization inside the ZBLAN spheres, we again relied on scanning electron microscopy. Figure 8 shows scans of inside surfaces of ZBLAN spheres that had been cracked open. Relying on SEM images by [7] (see Fig.9), we hoped to be able to see crystallization that may have formed during the re-solidification stage. Even though the SEM provided sub-micron resolution, no crystallization was apparent, see Fig. 10. However, the SEM's resolution was reduced by charging of the sample (since ZBLAN is insulating), so we might not be able to see the crystallization.

We considered scanning the sample with a low-intensity electron beam to leave enough time for the charges to flow off, but didn't have enough time on the SEM to understand how to do it. Another possibility was coating the ZBLAN with a very thin gold layer; however, it would have been very difficult to make the gold layer thin (less than 100 angstroms) and even enough to be able to resolve surface crystals after the coating.

Figure 8 confirms that overheating was a problem. The temperature

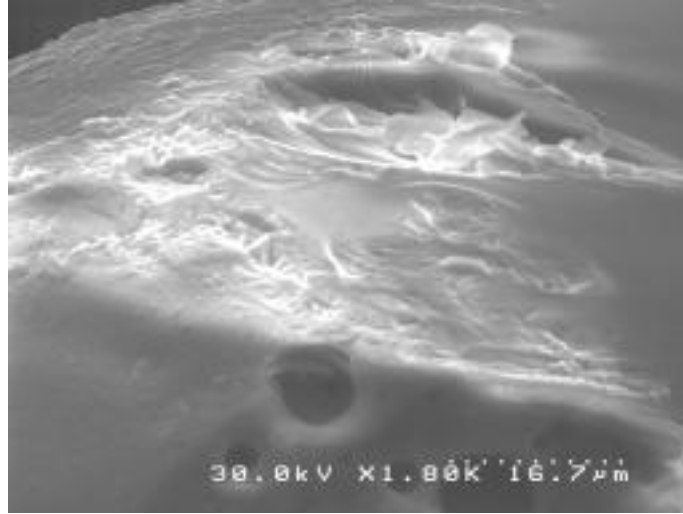


Figure 7: SEM image shows the charred surface of a ZBLAN microsphere.

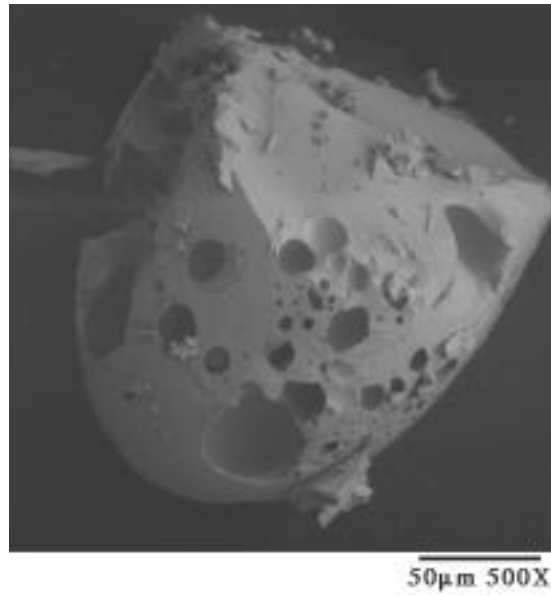


Figure 8: SEM images of inside of overheated ZBLAN microsphere.

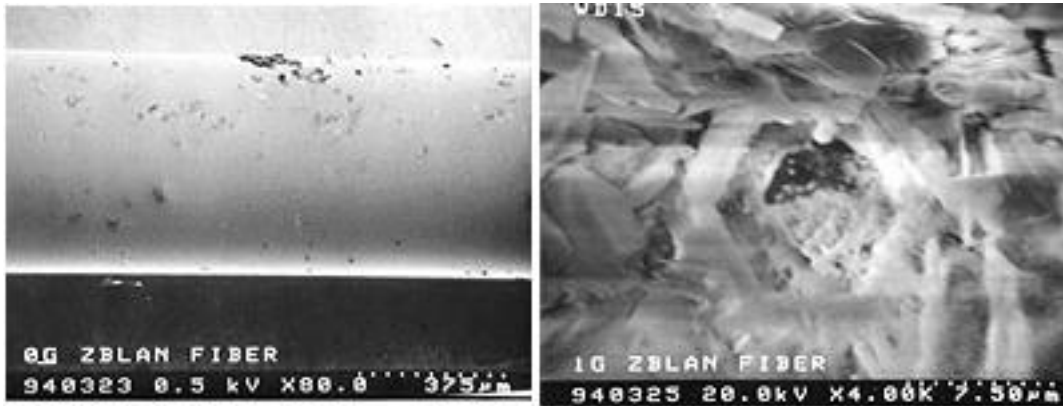


Figure 9: SEM images from Tucker et al.[7]. The ZBLAN sample produced on the left shows less crystallization than that on the right.

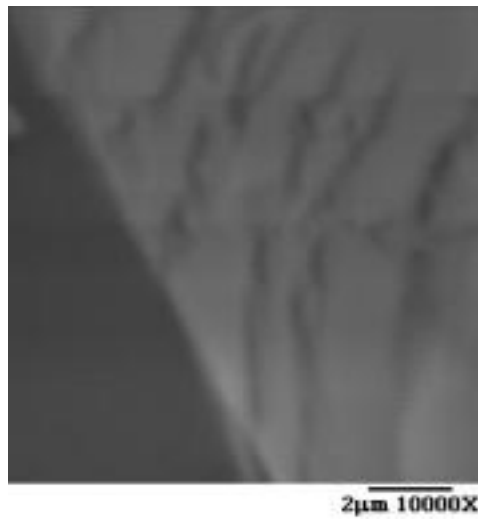


Figure 10: Charge-up of the sample is limiting the resolution. Offsets are introduced as the e-beam scans the sample.

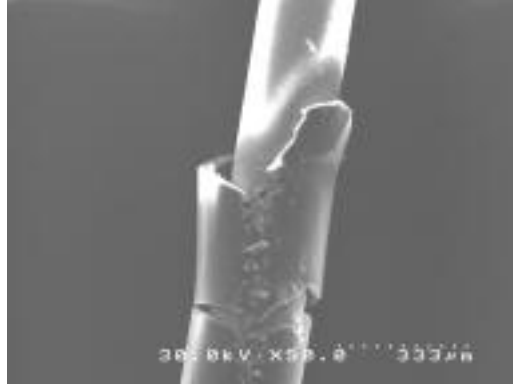


Figure 11: The etching procedures left some acrylate impurities on the fiber stems.

was hot enough to evaporate ZBLAN inside the stem, creating the bubbles clearly visible in the figure.

Figure 11 reveals a further problem: the fibers were not decladded completely in some areas. Such remaining bits of acrylate coating could have been heated together with the ZBLAN.

3 Results

The ZBLAN microspheres produced were not of sufficient quality to allow whispering gallery modes to be induced. Despite this shortcoming, the experiment was useful in uncovering several problem areas.

When the fibers were decladded, water from the air penetrated into the surface of the ZBLAN fibers. This caused reaction 1 to occur. When the fibers were heated to produce microspheres, the ZrO_2 sites mixed with the rest of the sample. Because ZrO_2 acts as a nucleation site at the surface, this process could be responsible for the milkiness of the ZBLAN spheres we produced.

Lastly, the temperature of the fiber splicer voltage arc was too high, evaporating parts of the ZBLAN sphere.

The silica control group of the experiment behaved as expected: there was no significant difference in the quality factors or shapes in silica-based microspheres produced in $0 \cdot g$ or in $1 \cdot g$. These microspheres had quality factors around $2 \cdot 10^8$.

4 Conclusions

This project points the way to a far improved second trial, one which will satisfy this list of added requirements:

- Surface contamination through exposure to oxygen and water in the air must be eliminated.
 - In the fiber preparation, use an etchant with very low water content. Test dichloromethane, nitric acid, and the HCl-based proprietary etchant from IFR, Inc.
 - After fiber preparation, remove adsorbed water in vacuum oven, vacuum dessicator, or plasma etcher.
- The heating method must be finely tunable so that the ZBLAN fibers are not heated much beyond the crystallization temperature.
 - Use platinum heating coil
 - Inert gas environment (N_2 or Ar)
 - Do not use Si-based spheres as they were already shown to behave the same in $0 \cdot g$ or in $1 \cdot g$.
- The experiment must be largely automated so that human interaction under the difficult conditions in microgravity is not required.
 - Produce board with series of identical coils to automate process on KC-135

5 Acknowledgments

We would like to thank our advisers at JPL, Lute Maleki and Vladimir Itchenko, who have really made this project possible. We appreciate their enthusiasm and willingness to help wherever they could.

Of course, funding also played a big role in making this project possible. Here again, we thank JPL. Further, we want to thank the Caltech physics department for its contribution, particularly its chair Dr. Tombrello for having confidence in the project.

We also want to thank Tobias Kippenberg and his adviser, Dr. Vahala, for letting us use the group's apparatus for Q measurements.

We are also in debt to Dr. Kortan at Bell for his interest and invaluable advice.

References

- [1] Griffel G, Serpenguezel A, and Arnold A, *1995 IEEE Symposium on Frequency Control* (Institute of Electrical and Electronics Engineers, New York, 1995).
- [2] von Klitzing W et al. *Very low threshold green lasing in microspheres by up-conversion of IR photons*, J.Opt.B: Quantum Semiclass. Opt. **2** (2000), pp 204-206.
- [3] Ming Cai, Oscar Painter, and Kerry Vahala, *Observation of Critical Coupling in a Fiber Taper to a Silica-Microsphere Whispering-Gallery Mode System*, Phys. Rev. Lett, **Vol. 85**(1), 74 (2000).
- [4] Vernooy DW, Ilchenko VS, Mabuchi H, Streed EW, and Kimble HJ, *High-Q measurements of fused-silica microspheres in the near infrared*, Optics Letters, **Vol. 23**(4), 247 (1998).
- [5] L.J. Moore et al, *Surface Crystallization of ZBLAN glasses*, Journal of Non-crystalline Solids, 1992.
- [6] *ZBLAN continues to show promise*, NASA Press Release, Feb 1998. http://science.nasa.gov/newhome/headlines/msad05feb98_1.htm
- [7] Tucker, Dennis. *ZBLAN Research Takes Step Forward*. June 3, 1997. <http://www.ssl.msfc.nasa.gov/msl1/themes/accomplishments.htm>
- [8] D Tucker *Effects of microgravity on ZBLAN optical fibers utilizing a sounding rocket*, SPIE Proc. 1996, **Vol. 2809**, 23.