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EFFECT OF MICROGRAVITY ON CRYSTALLIZATION OF ZBLAN FIBERS

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ZrF_4-BaF_2-LaF_3-AlF_3-NaF (ZBLAN) optical fiber was flown on board the NASA's KC-135 microgravity aircraft to determine the effects of microgravity on crystal growth in this material. Fiber samples were placed in evacuated quartz ampoules and heated to the crystallization temperature in 0g, 1g, and 2g. The 1g and 2g samples were observed to slump and crystallize. The 0g samples showed no evidence of crystallization.

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INTRODUCTION

Mid infrared fiber optics have many promising applications in both the military and industrial sectors. These include ultralong repeaterless transcontinental and transoceanic links, nuclear radiation resistant links, high capacity wavelength multiplexed fiber optic systems, remoting of infrared focal planes, infrared laser devices, infrared power delivery, long-length fiber optics sensor systems and nonlinear optical systems.[1] Heavy metal fluoride glasses have shown the most promise to date. The most stable heavy metal fluoride with respect to crystallization appears to be those in the ZrF_4-BaF_2-LaF_3-AlF_3-NaF family, commonly referred to as "ZBLAN" glasses.[2]

Intrinsic and extrinsic processes limit light propagation at low powers in ZBLAN.[3] Intrinsic processes include band gap absorption, Rayleigh scattering and multiphonon absorption. Extrinsic processes include impurities such as rare-earth and transistion metal ions and crystallites formed during fiber pulling. The theoretical loss coefficient for ZBLAN is 0.001 db/km at 2 microns. Achieving this lower limit is hampered by both the intrinsic and extrinsic processes.

All of the intrinsic processes and extrinsic impurities can be controlled through processing of the initial raw materials and in preparation of the glass preform. The devitrification of ZBLAN is due to a narrow working range and low viscosity at the pulling temperature.[4] These two factors make this glass unstable and prone to crystallization.

Microgravity processing offers the potential to minimize these losses in ZBLAN glass.[5] Improved purity of raw materials and the possibility of containerless processing in microgravity in the future are expected to expand the glass forming region and minimize the formation of microcrystallites during synthesis of this glass.[5] Microgravity processing also offers the potential of minimizing phase separation and crystallization during subsequent glass forming steps.[5] Fluoride glass synthesis has not been attempted to date due to the corrosive nature of the process.[5]

Canadian work indicated the enhanced crystallization of certain ZBLAN formulations under 2g and no evidence of crystallization in 0g using a T-33 aircraft.[5,6]

The purpose of this study was to verify the Canadian work and provide a springboard for studying crystallization of ZBLAN on a future shuttle flight.

EXPERIMENTAL

A two meter length of ZBLAN optical fiber (325 micron diameter) was obtained from Infrared Fiber Materials, Silver Springs, Maryland. The protective polymer coating was removed chemically, and then the fibers were cut into 6mm lengths. Individual fibers were placed in evacuated quartz ampoules and sealed.

A fiber annealing furnace (FAF) was designed and constructed for use on the KC135 microgravity aircraft. A drawing of the FAF is shown in figure 1. The FAF consists of a preheat furnace, annealing furnace and a quench block. The sample is translated manually through each component using a stainless steel push rod.
In operation, a single quartz ampoule would be placed at the end of the push rod, and then translated into the preheat furnace for a period of two minutes. This allowed the fiber to reach a temperature of 215°C. Then during either the microgravity portion of the parabola or the 2g portion, the ampoule would then be translated into the annealing furnace for 15 seconds allowing the sample to reach a temperature of 415°C. This temperature is approximately 15°C above the crystallization temperature for this ZBLAN glass. At the end of 15 seconds the ampoule would be translated into the copper cooling chamber, which was perforated, and water was used to quench the ampoule via a plastic syringe.

Ground tests were performed to determine the time necessary to reach the nucleation temperature and to run 1g studies. A thermocouple was inserted into a glass ampoule and then translated into the preheat furnace until the temperature reached 215°C and then into the annealing furnace until a temperature of 415°C was obtained. In this manner the times necessary for preheat and annealing during the parabolic manuever were obtained. Five samples of ZBLAN fiber enclosed in the ampoules were then heated in the apparatus as described above.

During the KC135 flight ten samples were heated during the 0g portion of the parabolic maneuver and ten samples during the 2g portion.

ZBLAN samples were examined using optical microscopy, scanning electron microscopy and EDX analysis. The samples heated in 0g were easily removed from the ampoules, however, the 1g and 2g samples slumped due to gravity. These samples were removed by first grinding halfway through the ampoule (lengthwise) and then removing with tweezers.

RESULTS AND DISCUSSION

An optical micrograph of a fiber processed in 0g is shown in figure 2. On the surface of the fiber there appear to be possible crystallites. Figure 3 is an SEM photograph of the same fiber again showing discrete particles on the fiber surface. EDX, figure 4, shows these particles to be composed of silica with some magnesium. This is most likely contamination from the quartz ampoule. The small peaks showing hafnium, barium, zirconium and fluorine are due to the beam penetrating the particle and striking the fiber below. Figure 5 shows the EDX spectra for the fiber itself. The hafnium is present due to it's presence in the fiber cladding material. Figure 6 shows a fiber processed at 1g still in it's ampoule. Note the opacity and slumping of the fiber. An SEM micrograph of the cross-section of this fiber is shown in figure 7. Figures 8 and 9 show higher magnification SEM micrographs of the 1g fiber. Individual crystals are evident from these two figures. Figure 10 is an EDX spectrum of one of the crystals. It is high in barium content as compared to the 0g fiber spectrum. Metastable and stable phases of beta - $BaZrF_6$ and beta - $BaZr_2F_{10}$ along with the higher temperature stable forms have been identified by other authors.[2,4] The crystals seen in figures 7 and 8 are most likely one of these phases.

The samples processed at 2g were identical in appearance to those processed in 1g.

From the above results it appears that microgravity would be beneficial to producing ZBLAN optical fibers. This is somewhat intuitive since ZBLAN has a low viscosity near the eutectic and the difference between the crystallization temperature and the glass transistion temperature is less than 100°C. Both of these reasons have been cited as causes for ZBLAN 's tendency toward crystallization. Both conditions plus the wide variation in atomic weights in ZBLAN would contribute to buoyancy convection which is suppressed in microgravity. Therefore one would expect little or no crystallization if the fiber could be produced in a microgravity environment.

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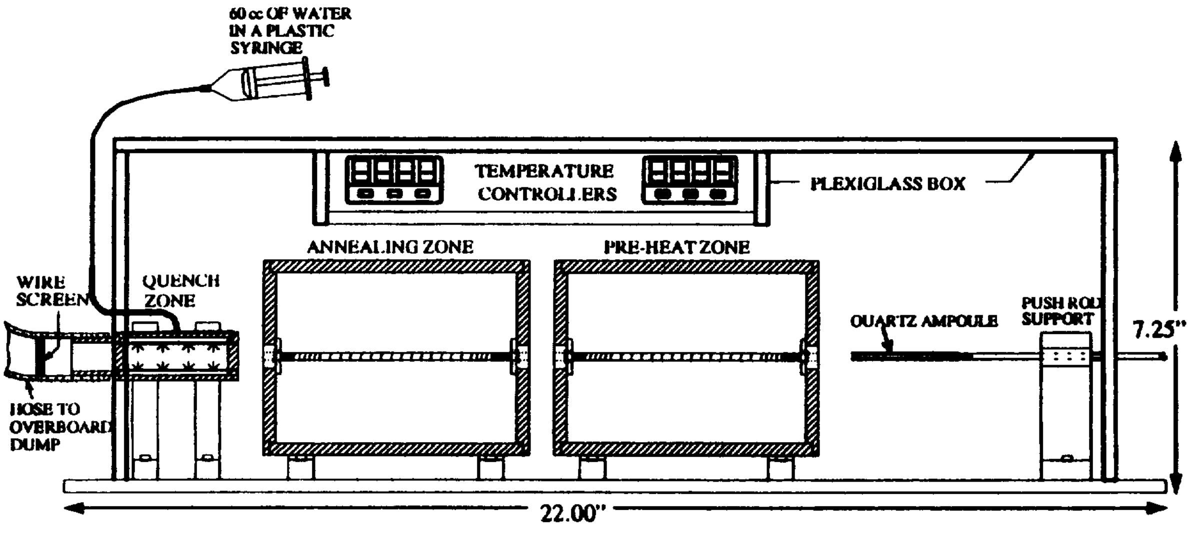

Figure 1. Schematic of Fiber Annealing Furnace

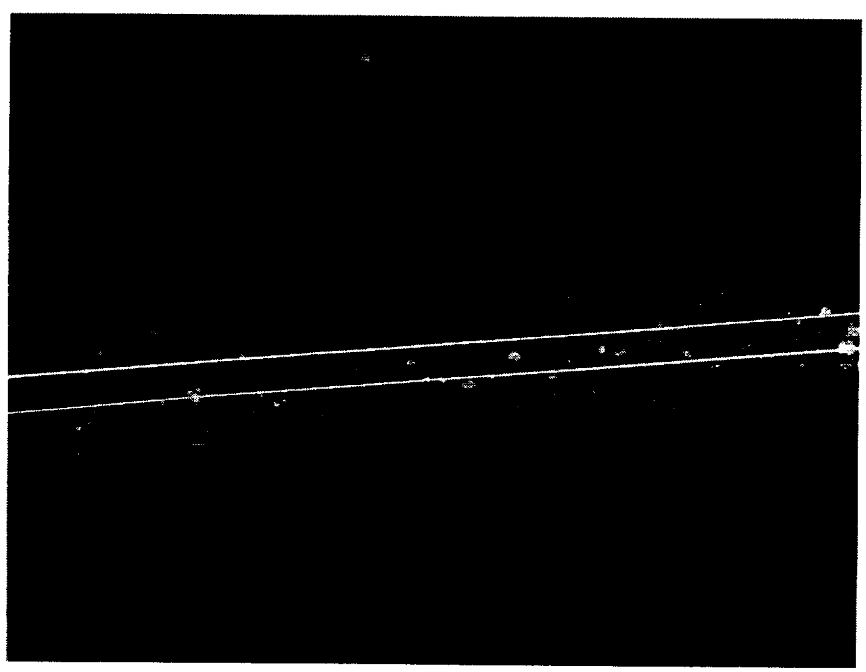

Figure 2. Optical Micrograph of 0g Fiber

Figure 3. SEM Micrograph of 0g Fiber

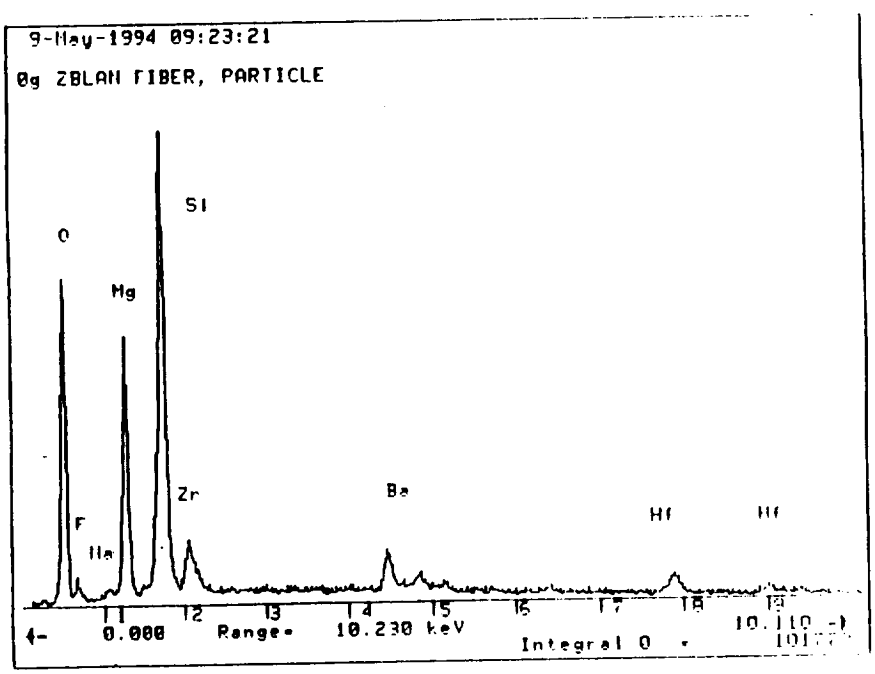

Figure 4. EDX of Particle on 0g Fiber

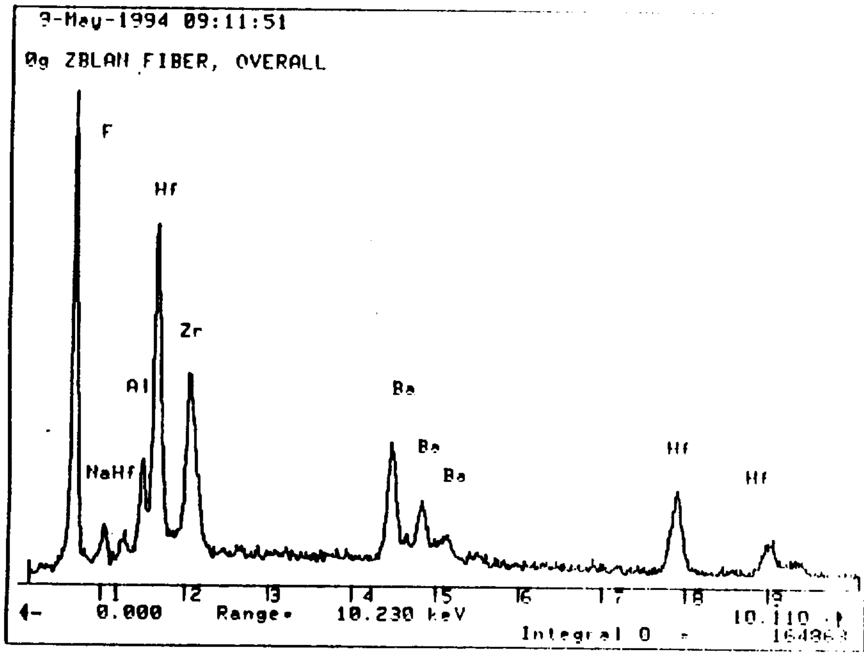

Figure 5. EDX of 0g Fiber

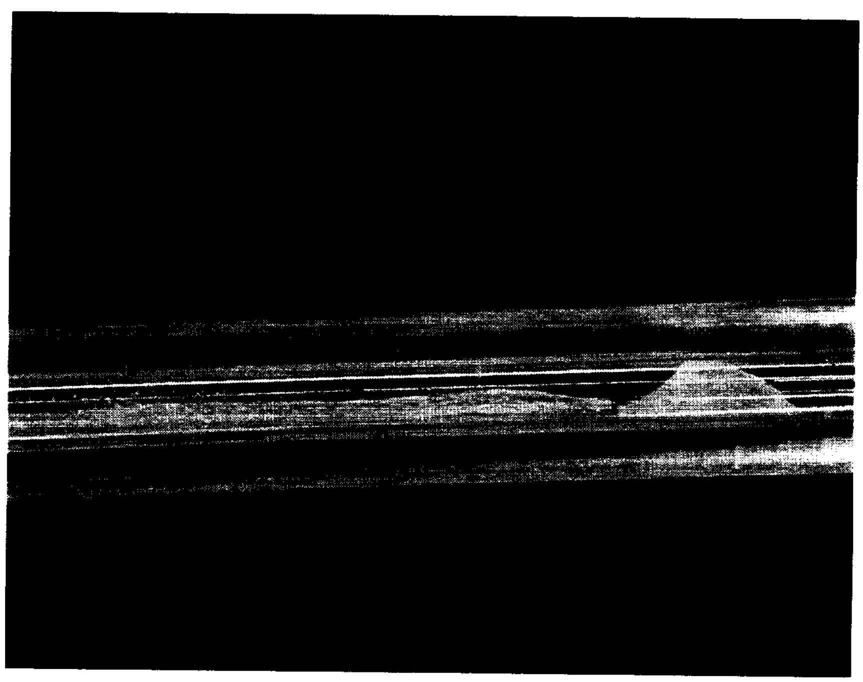

Figure 6. Optical Micrograph of 1g Fiber in Ampoule

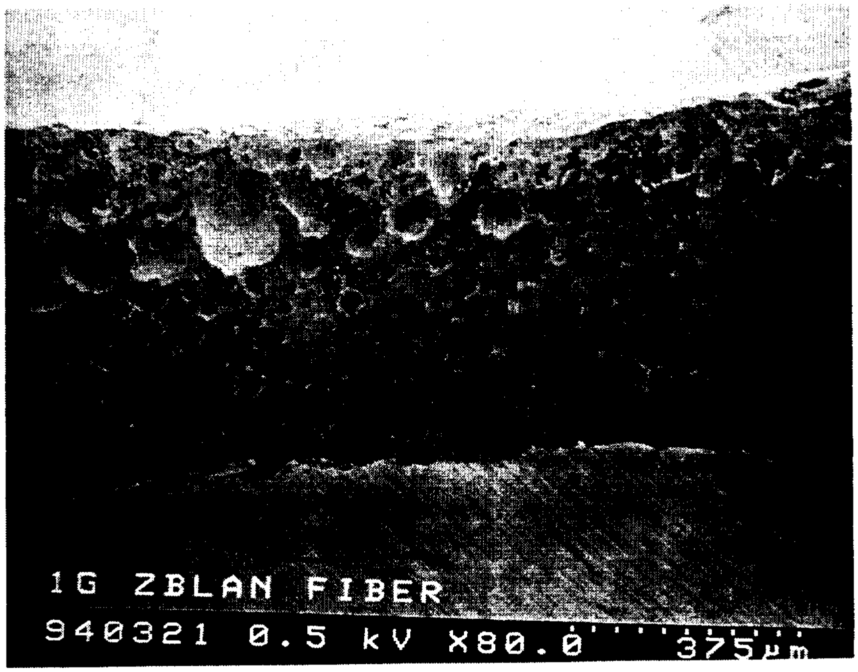

Figure 7. SEM Micrograph of 1g Fiber

Figure 8. SEM Micrograph of 1g Fiber at 1000x

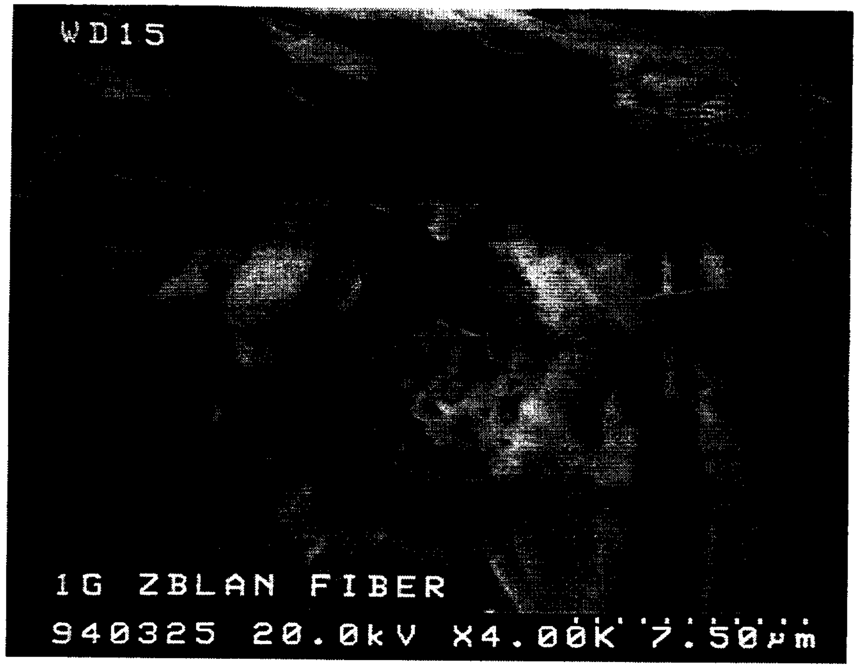

Figure 9. SEM Micrograph of 1g Fiber at 4000x

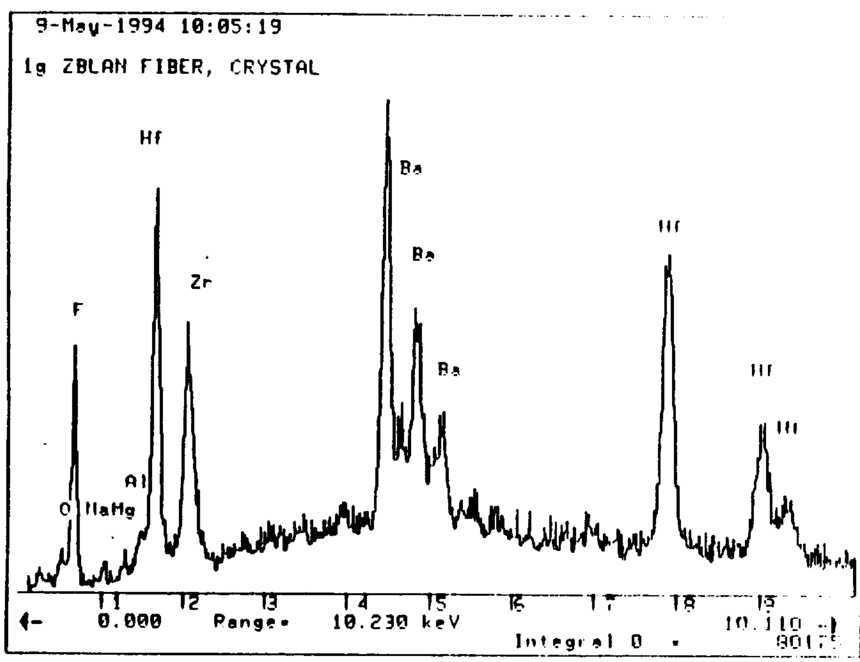

Figure 10. EDX Spectra of 1g Fiber Crystal

APPROVAL

EFFECTS OF MICROGRAVITY ON CRYSTAL GROWTH IN ZBLAN GLASS FIBER

By D.S. Tucker

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Classification Officer. This report, in its entirety, has been determined to be unclassified.

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