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Effect of gravity on crystallization in heavy metal fluoride glasses processed on the T-33 parabolic flight aircraft

S. VARMA
Supan Technologies Inc., 1877 Chaine Court, Orleans, ON, Canada K1C 2W6
E-mail: supantech@sprint.ca

S. E. PRASAD
Sensor Technology Ltd., 20 Stewart Road, P.O. Box 97, Collingwood, ON, Canada L9Y 3Z4

A. AHMAD, T. A. WHEAT
MTL/CANMET, Natural Resources Canada, 405 Rochester St., Ottawa, ON, Canada K1A 0G1

Heavy metal fluoride (HMF) glasses are prone to micro-crystal formation and resulting optical degradation during their high-temperature processing for fibre drawing. It is believed that the absence of gravity-driven density segregation in microgravity can reduce this undesired micro-crystallization during the processing of HMF glasses. Experiments were conducted on the T-33 parabolic flight aircraft in microgravity and under 2-g acceleration to study the effect of gravity on crystallization in HMF glasses. These preliminary experiments indicated that gravity enhances crystallization in HMF glasses during their processing at 370–400°C. However, these results were not considered conclusive due to the short duration of 20 seconds available on the parabolic flight aircraft. Subsequent ground-based experiments were conducted on the T-33 payload using statistical design of experiments to simultaneously study the effect of glass composition, processing temperature, processing time and mode of heating (continuous or pulsed). These experiments indicated that a continuous processing time of over two minutes at crystallization temperatures is required to observe a statistically significant amount of crystallization in HMF glasses. This established the need for longer duration experiments on the sounding rocket, space shuttle or space station.

1. Introduction

Optical communication systems currently utilize silica fibres which have achieved their theoretically predicted minimum optical loss of about 0.15 dB/km. Future applications will demand fibres with even lower losses. Heavy metal fluoride (HMF) glasses are amongst the most promising candidates for low loss optical fibre applications due to their theoretically predicted ultra-low optical loss of 0.001 dB/km in near-infrared region [1]. Unfortunately, in spite of over 25 years of extensive research, conventional processes have failed to realize the predicted low losses in HMF glass fibres. The losses generally obtained in HMF glass fibres are in the range of 1–10 dB/km, with the lowest reported value being 0.65 dB/km [2].

The primary cause for higher than predicted losses in HMF glass fibres is believed to be excess scattering from micro-crystals formed during glass synthesis and fibre drawing. These micro-crystals can be formed by heterogeneous or homogeneous nucleation. Contamination of the glass melt from the processing container is the primary source for heterogeneous nucleation, while gravity-driven density segregation is believed to be the main cause for homogeneous nucleation in viscous HMF glass. Since both these factors cannot be removed during the conventional processing of HMF glasses and fibres on the ground, formation of these micro-crystals can not be avoided. This has been identified as the limiting factor in the development of low loss HMF glass fibres [3].

HMF glass fibres are produced by a two-step process involving: (i) synthesis of bulk glass preforms by a melt-quenching technique, and (ii) fibre drawing from these preforms at a temperature where their viscosity is in the range of 10^3–10^4 dPa.s [4]. The microgravity environment of space offers the potential for containerless processing of HMF glasses and fibres in the absence of strong gravitational force. This can offer numerous advantages during both the high-temperature process steps involved in bulk HMF glass synthesis and fibre drawing [5]. Microgravity may, in fact, hold the key for eventually realizing the predicted ultra-low losses in HMF glass fibres by minimizing crystal nucleation.

HMF glass synthesis produces corrosive and toxic fumes from the melt and is not a desired process in space. But HMF glass fibre drawing can be easily done

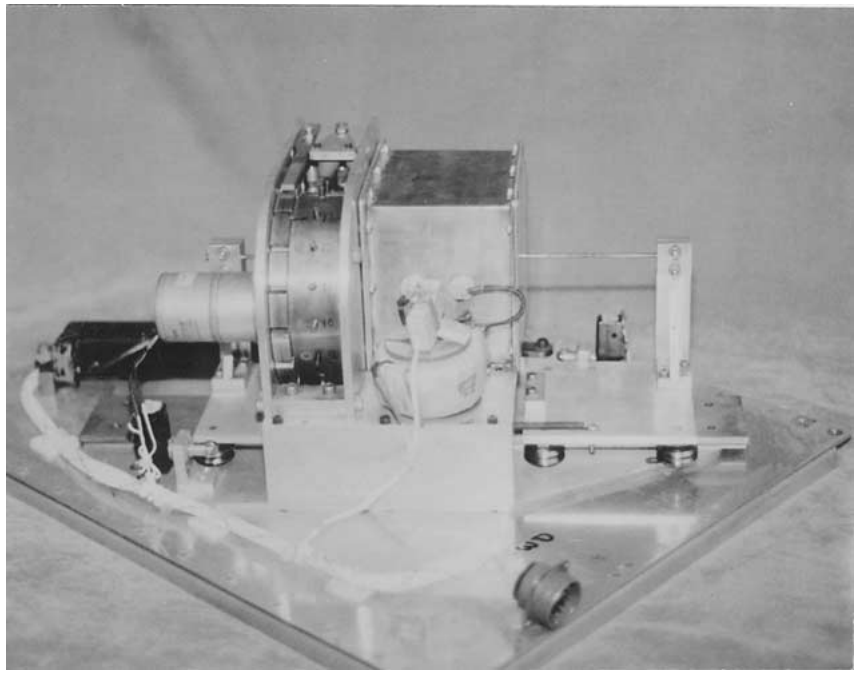

Figure 1 The material processing system of the T-33 payload.

in space since the glass preform is reheated to its viscous state without reaching its molten state and no corrosive and toxic fumes are produced. In fact, it is not essential to use microgravity environment during both the glass synthesis and fibre drawing steps to realize its benefits. The use of microgravity during fibre drawing alone can be beneficial. It has been reported that even if a HMF glass sample is synthesized in a container on the ground and contains heterogeneous nuclei, such nuclei remain confined to the region near the surface of the sample during subsequent remelting in microgravity. The absence of buoyancy convection in space limits the transport of heterogeneous nuclei to the bulk of the molten glass sample, which results in improved homogeneity in the bulk of the glass sample [6]. This could reduce crystallization in the glass during its reheating for fibre drawing.

The focus of our research is on studying the effect of gravity on crystallization and/or optical degradation in HMF glasses during their heat treatment for fibre drawing. HMF glass samples in our research were synthesized on the ground and then heat treated in microgravity. This paper describes a payload developed for the processing of HMF glasses on the T-33 parabolic flight aircraft, provides experimental details, and discusses the results obtained from crystallization experiments conducted on the ground, in microgravity and in 2-g acceleration.

2. The T-33 material processing payload

This payload was developed in-house for the high-temperature processing of materials on the T-33 parabolic flight aircraft of the National Research Council (NRC) of Canada in Ottawa. The T-33 aircraft is a two seater fighter training jet modified for microgravity experiments, in which the back seat is removed to accommodate the experimental payload. Since there was no room for a payload operator, a completely automated payload was developed for these experiments.

The T-33 payload consisted of a material processing system, a control system using a programmable logic control (PLC) module, and a remote pilot console. Each of these were housed in separate boxes. The control system box sat on top of the material processing box, forming its lid, while the remote pilot console was mounted in the cockpit. The payload operated on a 28 VDC power supply from the aircraft. It could be operated in either a manual or an automatic mode. A separate power supply was used for ground-based operation of the payload. A broad range of experimental conditions could be preprogrammed in the PLC controller to suit the processing of various materials such as glasses, ceramics, metals, etc.

The material processing system of the T-33 payload is shown in Fig. 1. It consisted of a resistance heated furnace capable of operating up to 1000°C, an eight chamber rotatable magazine which operated both as a storage unit and a quench block, and the sample insertion and retrieval mechanism. The furnace temperature was preset and controlled by a programmable PID controller located in the control system box. The payload could process up to 8 samples per flight, whose dimensions (including encapsulation) were limited to 3 mm (D) $\times$ 50 mm (L). The HMF glass samples were sealed in fused silica capsules making the system safe for handling corrosive materials during their processing. As an added precaution, the material processing system was continuously evacuated by the aircraft's venturi pump to remove any fumes that may accidentally develop during the experiment.

The control system facilitated the automatic operation of the payload through the remote pilot console mounted in the cockpit. The system had eight analog inputs and eight digital I/O lines which permitted data acquisition and control operations. A digital

counter, which could be reset prior to each flight, displayed the number of loading and unloading cycles the system had gone through. This was used to index the samples.

The pilot console was equipped with a start (event) switch, a man/auto selector switch, an abort switch, a sample jam indicator light, an over temperature warning light, a temperature OK indicator light, a manual mode indicator light, an automatic mode indicator light and a cycle complete indicator light.

The automatic mode was meant for the processing of samples during the flight or on the ground using a preset cycle. In this mode, upon receiving an event signal from the pilot console, a sample was automatically loaded from the magazine into the furnace and processed at the preset temperature for 20 seconds. It was then unloaded into its chamber in the magazine. The magazine then rotated by one chamber to bring the next sample to the loading position. The cycle counter advanced by one, and the system waited for the next event signal.

The manual mode was meant for longer duration ground based experiments, and the loading and unloading of samples before and after each flight. In the manual mode, each sample was loaded into and unloaded from the furnace via separate push buttons on the control system panel. The magazine was rotated by one chamber at a time by pressing the index switch. The process time was thus controlled by the operator.

3. Experimental details

3.1. Preparation of HMF glass samples

The most widely studied HMF glass system is called ZBLAN glass, since it consists of ZrF_4, BaF_2, LaF_3, AlF_3, and NaF. Often LaF_3 can be replaced with GdF_3 to form a ZBGAN glass. We synthesized glass samples of two compositions from each of these glass systems for this research. These compositions are given in Table I in terms of mol% of the fluorides. ZBLAN-L4 glass is the most commonly used composition in HMF glass fibres, while the other compositions were used to study the affect of glass composition on crystallization in these glasses.

HMF glass samples were synthesized by a conventional melt-quenching technique using "Fibre Grade" fluoride precursors from BDH Chemicals. Typically a 50 g charge was melted in a platinum crucible in an argon atmosphere using a resistance heated furnace. The melt was quenched in a pre-heated graphite mould to form a glass preform, which was then annealed to remove thermal stresses. Although good quality HMF glass preforms in various sizes and shapes were routinely synthesized by this process, cylindrical preforms of about 6 mm (D) $\times$ 50 mm (L) were produced for this research. The graphite mould left a carbon film at the surface of glass preforms, which was removed by mechanical polishing.

Thin filaments (about 1 mm dia) of HMF glasses were used for the T-33 experiments. These were drawn from the cylindrical preforms by softening their centre in a customized furnace and pulling the ends outwards with uniform speed. These filaments were cut into about 40 mm long pieces, and were individually sealed in silica tubes of 3 mm (OD) $\times$ 50 mm (L).

TABLE I Composition of HMF glasses used in this research (in mol% $\pm$ 0.1%)

	ZBLAN		ZBGAN	
Raw materials	L4	L8	G4	G8
ZrF_4	53	50	50	47
BaF_2	20	19	22	21
LaF_3	04	08	–	–
GdF_3	–	–	04	08
AlF_3	03	03	04	04
NaF	20	20	20	20

3.2. T-33 flight experiments

Preliminary crystallization studies on HMF glass samples were conducted onboard the NRC's T-33 parabolic flight aircraft in Ottawa in 1990–91 [7]. These experiments were conducted in microgravity, on the ground and under 2-g acceleration condition. Due to the short processing time of only 20 seconds, there was a strong possibility that ground-based processing might not produce any crystallization in HMF glasses. Therefore, it was decided to process some glass samples in 2-g acceleration also to enhance the potential effect of gravity. Four processing temperatures were used in the range of 370–500°C. The furnace maintained its temperature to within $\pm$ 1°C of the set-point. Eight encapsulated HMF glass samples were processed at one pre-set temperature on each of the T-33 aircraft flights. The first four samples were processed in microgravity, while the last four were processed in 2-g. The ground-based experiments were done on the same payload using the same automatic process cycle.

Prior to the flight, HMF glass samples were loaded into the magazine of the material processing system. The temperature controller was set at the desired processing temperature. The payload was installed on the back seat of the aircraft and connected to the 28 VDC power supply of the aircraft. During the flight, the pilot took the aircraft either through a vertical parabolic loop to attain microgravity condition for about 20–25 seconds, or took it through a horizontal loop with appropriate pull to attain an acceleration level of 2-g for about a minute. The acceleration data was recorded by the aircraft flight data recorder. A typical parabolic flight profile of an aircraft to achieve microgravity is shown in Fig. 2.

During the flight, the pilot only utilized the remote console to operate the payload in its automatic mode. Before initiating the aircraft manoeuver to go into microgravity or 2-g pull loop, the pilot ensured that the man/auto selector switch on the console was in its auto position, and the automatic mode indicator and temperature OK indicator lights were ON. If ever the over temperature indicator light remained ON, the pilot waited for some more time to allow the temperature controller to stabilize the furnace temperature. Once in microgravity or 2-g loop, the pilot activated the event start

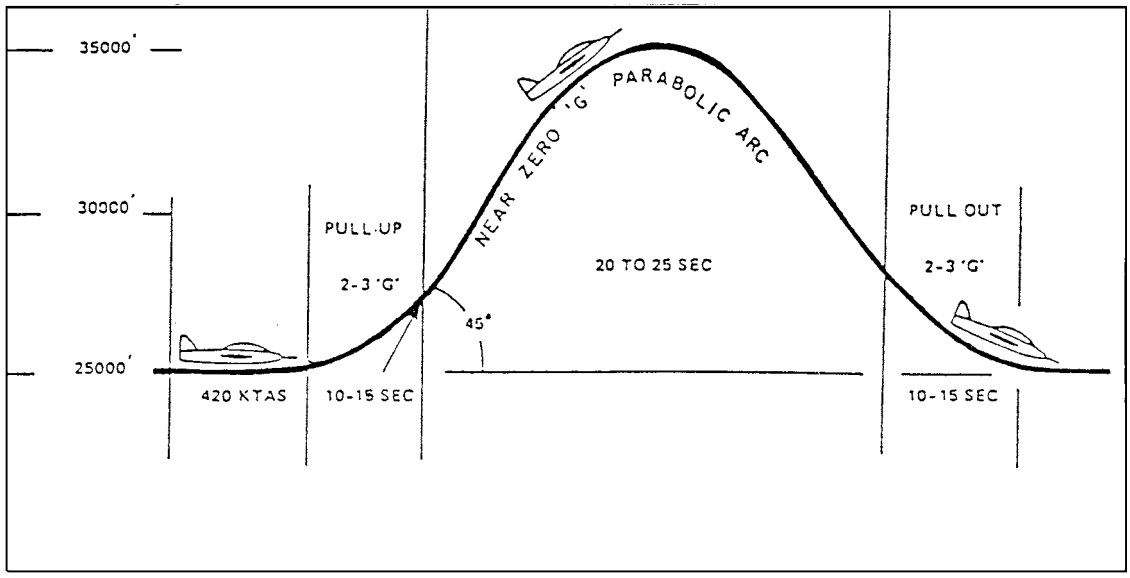

Figure 2 A typical parabolic flight profile of an aircraft to achieve microgravity.

switch to initiate the automatic process cycle, which was described earlier. A successfully completed process cycle was indicated by the cycle end indicator light. This sequence was repeated eight times during a flight to process all eight HMF glass samples. If the sample jam indicator light came on (due to mechanical failure in the sample insertion and retrieval system) or the pilot encountered any unexpected problem, he aborted the experiment and returned to the base.

3.3. Ground-based experiments under statistical design

The short microgravity processing time of 20 seconds was not considered adequate for meaningful crystallization experiments on HMF glasses. Moreover, glass composition, processing temperature and processing time were also expected to have an effect on crystallization. Longer processing onboard the T-33 aircraft was possible only through successive pulsed cycles of 20 seconds on the same sample. But the effectiveness of such successive pulsed heating cycles on the same sample during the T-33 flight experiments was questionable. Of course, the manual mode of the T-33 payload could be used on the ground for continuous heating of these glasses for a longer duration. Hence, ground-based experiments were conducted on HMF glasses under a statistical design [8] to simultaneous study the effect of glass composition, processing temperature, processing time and mode of heating on crystallization in these glasses.

This ground-based study utilized only 16 treatment combinations (TC's). The variable process parameters were: composition (L4, L8, G4 and G8), temperature (340, 375, 390 and 400°C), time (40, 120, 300 and 600 sec), and mode of heating (pulsed or continuous). The extent of crystallization in HMF glass samples was used as the response for statistical analysis of experimental data.

3.4. Sample characterization

As-synthesized HMF glass preforms as well as thin filaments used for these experiments were visually inspected to detect any bubbles, voids, particulate matter inclusions and crystallization in the samples. Only the samples free from any visual defect were used for these experiments.

Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) plots for HMF glasses in all four compositions were obtained by a Shimadzu DTA 50/TGA 50 system. These were used to determine temperatures for glass transition, on-set of crystallization, melting, as well as any chemical decomposition. The typical sample size were 10 mg, the N_2 flow was 40 ml/min, the heating rate was 10°C/min, and the temperature range for measurements was from room temperature to 550–600°C.

Structural characterization of a ZBLAN-L8 glass sample, before and after crystallization, was done by the powder X-ray diffraction method to identify its crystallized phases. A Rigaku powder diffractometer with Cu-K_α radiation ($\lambda = 1.5418$ Å) and a graphite monochromator was utilized for this purpose. The scan rate was 4°/min while the X-ray power was 55 kV/180 mA. The crystallized sample was obtained by heating the glass sample at 400°C for 1 hr.

Microstructural characterization of HMF glass samples, before and after their processing for crystallization studies, was done by a back scattered electron imaging technique using a JEOL-820 scanning electron microscope (SEM) operated at 15 kV with a beam current of 1–12 nano amperes. This SEM was equipped with a Tracor Northern solid state X-ray energy dispersive spectrometer. The energy dispersive X-ray analysis (EDXA) technique was used for elemental analyses of the host glass matrix and precipitated crystallized phases. The samples were mounted in an epoxy block, lapped parallel to their longitudinal axes up to the middle cross section and then polished on a lead lap using loose diamond and light oil.

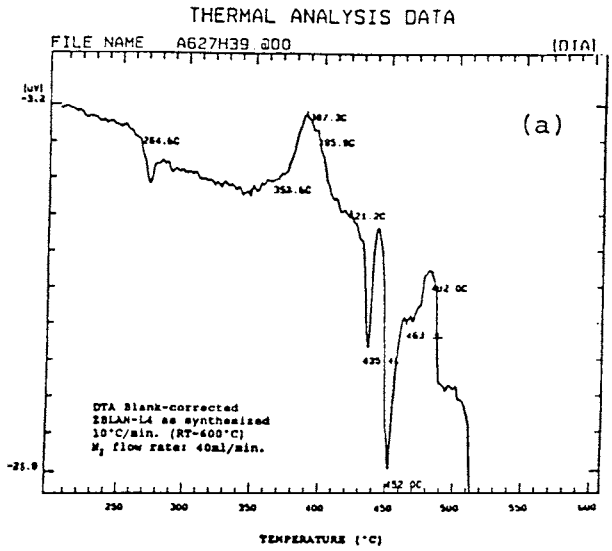

Figure 3 DTA plot for a ZBLAN-L4 glass sample.

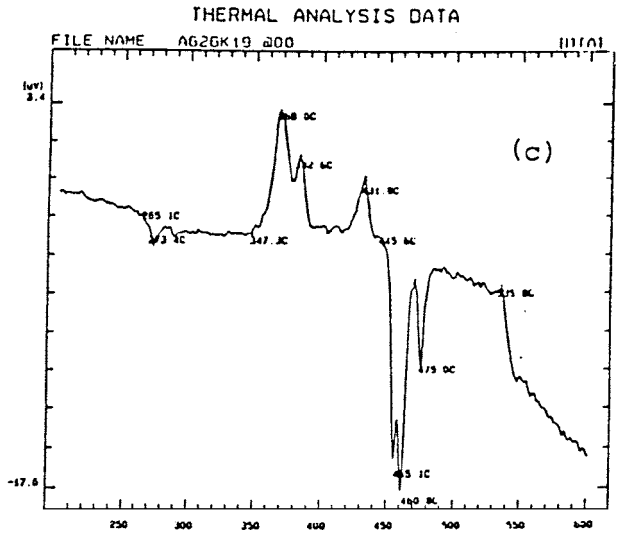

Figure 5 DTA plot for a ZBGAN-G4 glass sample.

4. Results and discussions

4.1. Visual inspection of glass samples

Good quality HMF glass preforms were synthesized for this research. Visually, they appeared clear, transparent and generally free of defects. Tiny bubbles were sometimes seen along the axis in some portions of the glass preforms and these portions were sliced off and discarded.

4.2. Thermophysical characterization

Figs 3 to 6 show the DTA plots for ZBLAN-L4, ZBLAN-L8, ZBGAN-G4, and ZBGAN-G8 glass samples respectively. These DTA plots indicated the presence of a number of endothermic and exothermic peaks.

Fig. 7 shows a TGA plot for a ZBLAN-L4 glass sample, which indicated no weight loss or decomposition in the sample till after its melting temperature. HMF glass samples in the other three compositions had similar TGA plots. The absence of any decomposition during the TGA measurements meant that the peaks observed

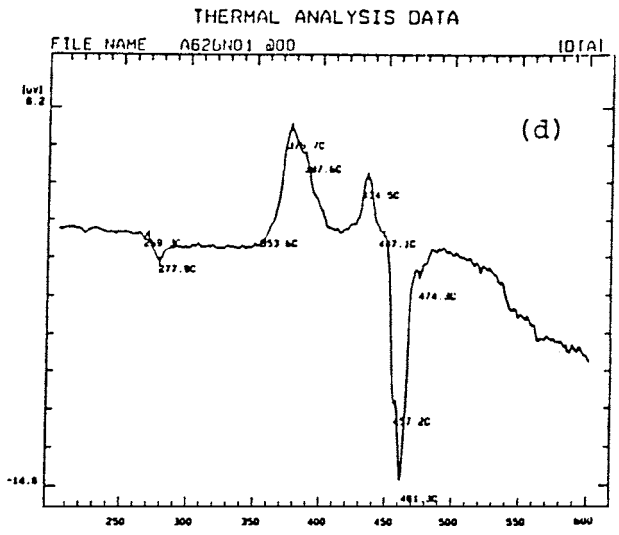

Figure 6 DTA plot for a ZBGAN-G8 glass sample.

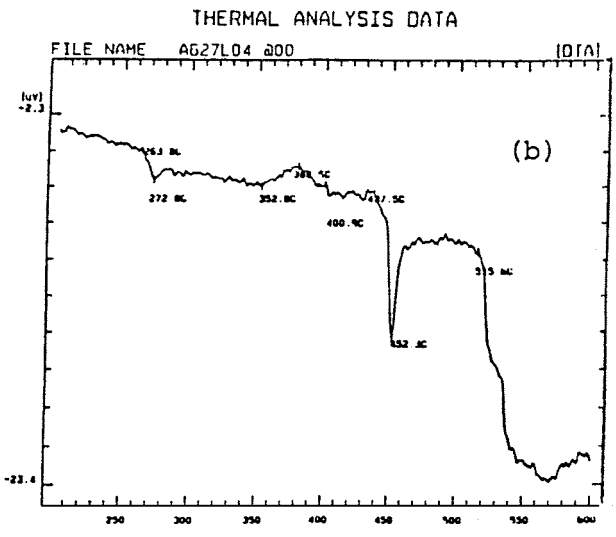

Figure 4 DTA plot for a ZBLAN-L8 glass sample.

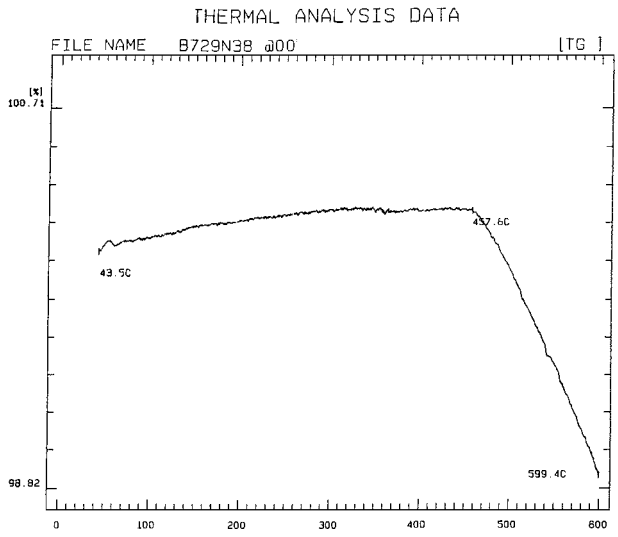

Figure 7 TGA plot for a ZBLAN-L4 glass sample.

TABLE II DTA data for HMF glasses obtained at a heating rate of 10°C/min

Thermophysical characteristics	ZBLAN		ZBGAN	
	L4	L8	G4	G8
	(Temperature in °C ± 1°C)			
Glass transition	265	264	265	269
Onset of crystal.	354	353	347	354
Crystal. peak 1	387	381	368	377
Crystal. peak 2	396	–	383	388
Crystal. peak 3	–	–	432	435
Onset of melting	421	438	446	447
Melting peak 1	435	452	455	457
Melting peak 2	463	–	461	461
Melting peak 3	–	–	475	474

in the DTA plots were due to physical processes such as glass transition, crystallization and melting.

The above DTA plots indicated that the crystallization in these HMF glass samples was affected by their composition. The ZBLAN-L4 glass sample had two overlapping crystallization peaks and two melting peaks implying the crystallization of two main phases. The ZBLAN-L8 glass sample showed only one crystallization and one melting peak implying the crystallization of only one major phase. On the other hand, both the ZBGAN glass samples indicated the presence of three crystallization and three melting peaks implying the crystallization of three major phases. Moreover, some minor phases could also have crystallized in all these HMF glass samples, which were probably hidden by the observed peaks for major phases.

Table II summarizes the temperatures for glass transition, onset of crystallization, crystallization peaks, onset of melting, and melting peaks, as obtained in these HMF glasses from the DTA plots. The glass transition in these HMF glasses was found to be in a narrow temperature range of 264-269°C, while the onset of crystallization was also in a narrow temperature range of 347–354°C. The onset of melting was in the range of 421–438°C for both ZBLAN glasses, while it remained the same (about 447°C) for both ZBGAN glasses.

4.3. Identification of crystallized phases

Fig. 8 shows the X-ray powder diffraction plots obtained on a ZBLAN-L8 glass sample in its as-synthesized state, as well as after its heat treatment for crystallization at 400°C for an hour. The as-synthesized glass sample was clearly amorphous in nature as indicated by two very broad and shallow peaks in the X-ray powder diffraction plot. The corresponding "d" values were 3.519Å and 1.953Å. But the crystallized sample showed many sharp diffraction peaks. Identification of these peaks by matching "d" values with the available data for various compounds revealed the presence of four crystallized phases: $BaZrF_6$ (β) as the major phase, $Na_7Zr_6F_{31}$ and $BaZrF_6$ (α) as minor phases, and $Ba_3Al_2F_{12}$ in traces.

4.4. Effect of gravity on crystallization

The first set of T-33 flight experiments involved ZBLAN-L4 glass samples, since this is the most commonly used composition in HMF glasses. These experiments indicated that heat treatment of ZBLAN-L4 glass samples at 370°C for 20 seconds in microgravity did not produce any crystallization, as indicated by the SEM micrograph of one such sample in Fig. 9. However, processing of other glass samples at 370°C

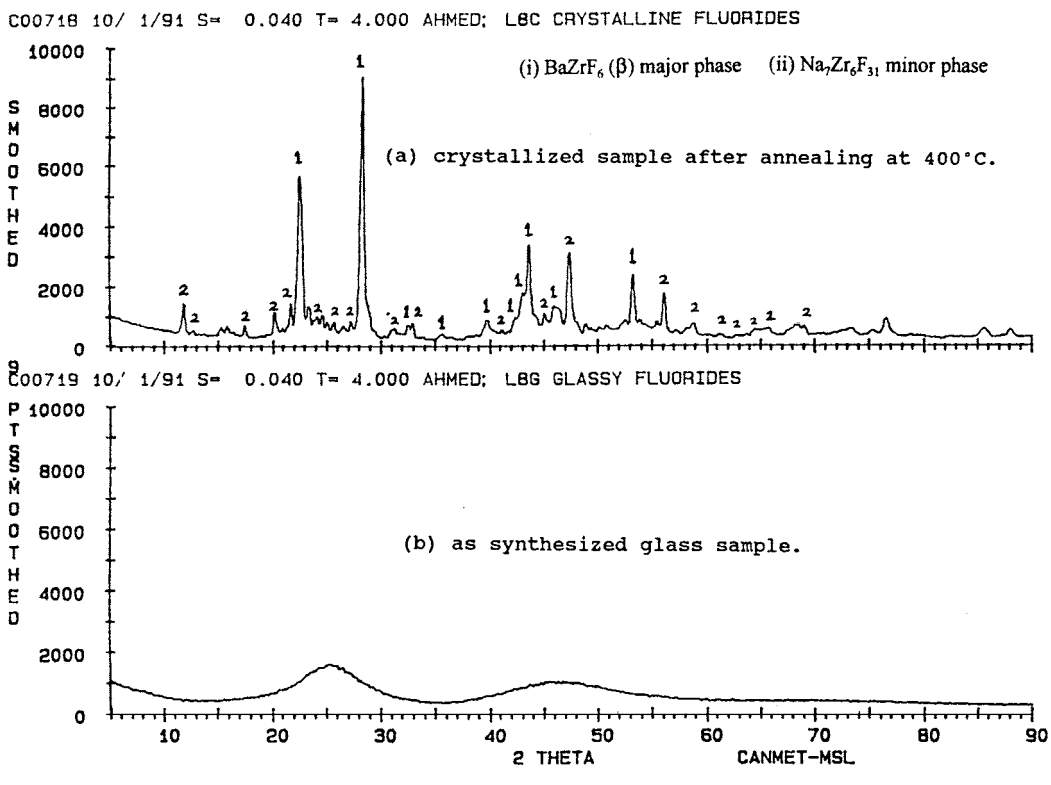

Figure 8 X-ray diffraction plots for a ZBLAN-L8 glass sample: (a) after crystallization due to heat treatment, and (b) in as-synthesized state.

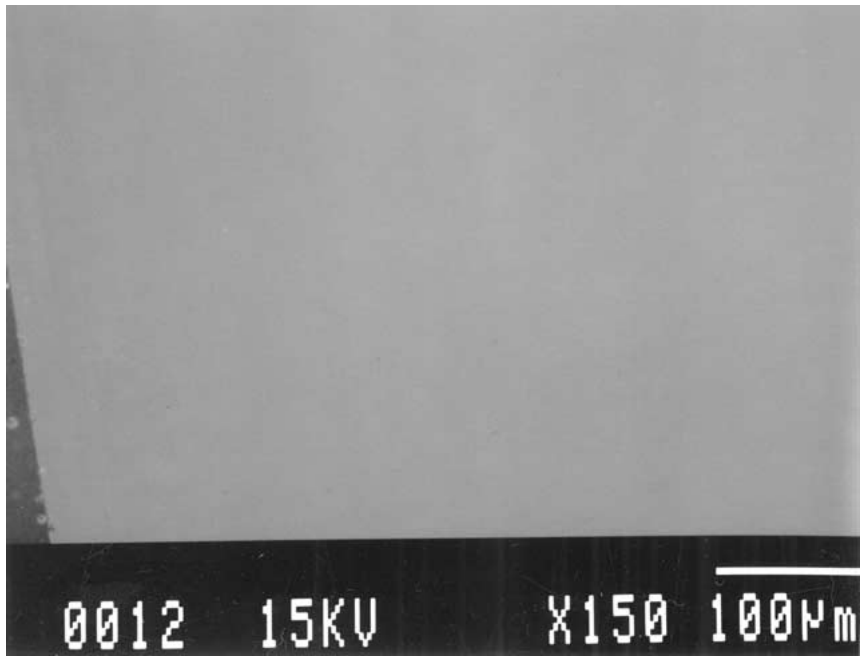

Figure 9 SEM micrograph of a ZBLAN-L4 glass sample processed at 370°C for 20 seconds in microgravity on the T-33 aircraft.

for 20 seconds in 2-g acceleration showed crystallization of two phases at the surface, as indicated by the SEM micrograph of one such HMF glass sample in Fig. 10.

Similar results were also obtained in other ZBLAN-L4 glass samples processed at 400°C. However, samples processed at temperatures of more than 420°C did not show any crystallization as they appeared melted and resolidified. The above results suggested that gravity enhances crystallization in HMF glasses during their heat treatment at crystallization temperatures.

The other three HMF glass compositions did not produce any crystallization after their processing on the T-33 aircraft either in microgravity or in 2-g acceleration. This was probably due to lower crystallization tendency in these compositions compared to ZBLAN-L4 glass and inadequate processing time of these experiments, as was determined by ground-based experiments discussed later.

Figs 11 to 13 present the EDXA spectra of different regions of the ZBLAN-L4 glass sample, whose SEM micrograph is shown in Fig. 10. The EDXA spectrum presented in Fig. 11 confirmed the presence of Zr, Ba (La?), Al and Na elements in the glass matrix. The La peaks are usually masked by the Ba peaks and can not be detected in these materials. Fig. 12 confirmed the presence of Zr and Ba

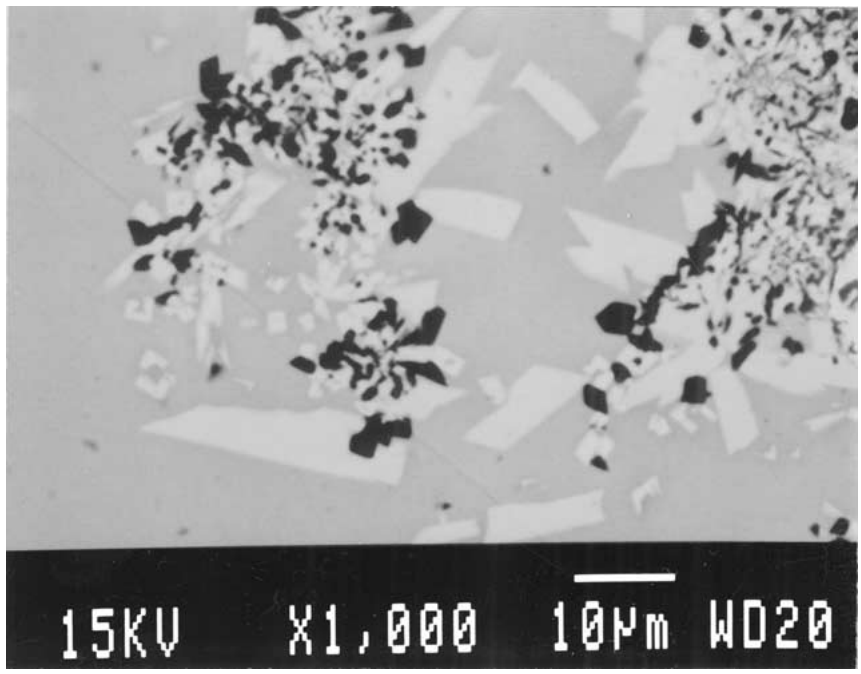

Figure 10 SEM micrograph of a ZBLAN-L4 glass sample processed at 370°C for 20 seconds in 2-g acceleration on the T-33 aircraft.

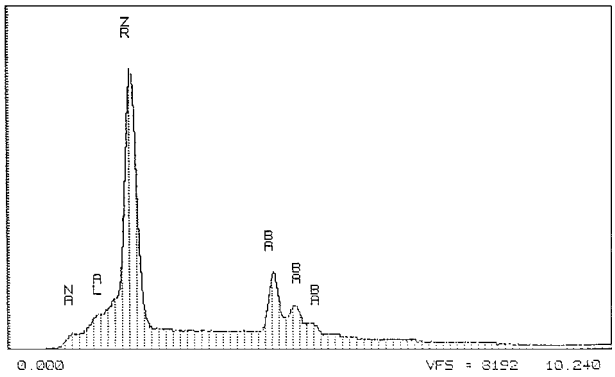

Figure 11 EDXA spectrum of the glass matrix in ZBLAN-L4 glass sample processed at 370°C for 20 seconds in 2-g acceleration, showing the presence of Zr, Ba (La?), Al and Na elements.

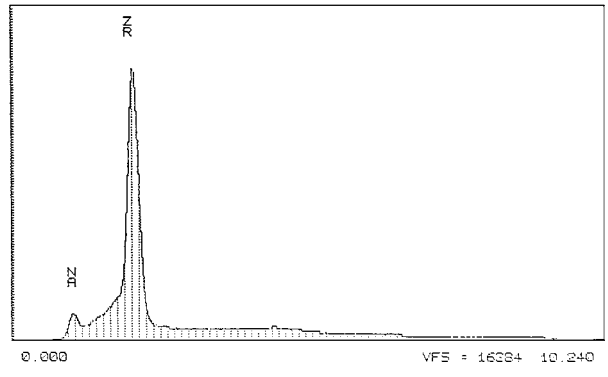

Figure 13 EDXA spectrum of the minor crystallized phase in ZBLAN-L4 glass sample processed at 370°C for 20 seconds in 2-g acceleration, showing the presence of Zr and Na elements.

elements in the major crystallized phase. This agreed with the earlier findings of the powder X-ray diffraction of a crystallized ZBLAN-L8 sample, which identified $BaZrF_6$ (β) as the major crystallized phase. Fig. 13 confirmed the presence of Zr and Na elements in the minor crystallized phase, which was also identified earlier as the $Na_7Zr_6F_{31}$ phase in the crystallized ZBLAN-L8 sample by the powder X-ray diffraction technique.

In order to independently verify the effect of gravity on crystallization in HMF glasses, which was an important finding of our T-33 experiments, D.S. Tucker conducted further experiments on the KC-135 aircraft in 1994 using ZBLAN-L4 glass fibres produced by two commercial suppliers. He also did not observe any crystallization in HMF glass samples processed in microgravity at 400°C for 20 seconds, while samples processed on the ground using the same processing cycle developed crystallization [9].

Thus, the results from these short duration experiments on the processing of HMF glasses onboard the parabolic flight aircraft indicate that gravity indeed enhances crystallization in these glasses. Therefore, use of microgravity during HMF glass fibre drawing could help in reducing commonly observed crystallization and/or resulting optical degradation in HMF glasses. This could lead to the long awaited realization of predicted ultra-low losses in HMF glass fibres.

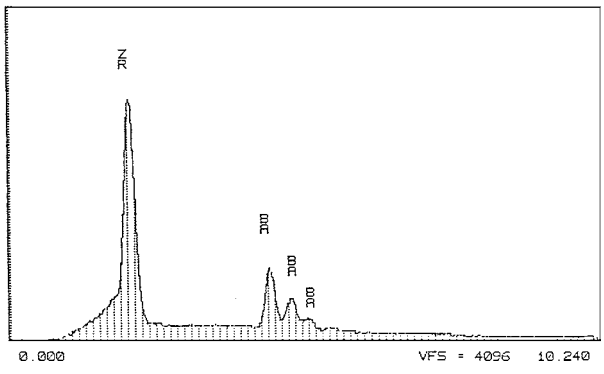

Figure 12 EDXA spectrum of the major crystallized phase in ZBLAN-L4 glass sample processed at 370°C for 20 seconds in 2-g acceleration, showing the presence of Zr and Ba elements.

4.5. Effect of other processing parameters on crystallization

Due to the short processing time of only 20 seconds, the results from the above parabolic flight experiments were not considered conclusive. Hence, statistically designed experiments were subsequently conducted on the ground using the T-33 payload to simultaneously investigate the effect of glass composition, processing temperature, processing time and mode of heating on crystallization in HMF glasses. Fig. 14 shows these factor effects as: (a) glass composition, (b) processing temperature, (c) processing time, and (d) mode of heating.

The results shown in Fig. 14a indicated that on an average, ZBLAN-L4 glass samples had the highest amount of crystallization, ZBGAN-G8 and ZBLAN-L8 glass samples produced the least amount of crystallization, while ZBGAN-G4 glass samples had roughly half the average crystallization produced by ZBLAN-L4 glass samples. This implied that ZBLAN-L4 glass samples had the highest rate of crystallization, which explained why only ZBLAN-L4 glass samples could develop detectable amount of crystallization during the short duration experiments on T-33 aircraft in 2-g.

Fig. 14b indicated that the extent of crystallization increased rapidly from 340 to 375°C in HMF glass

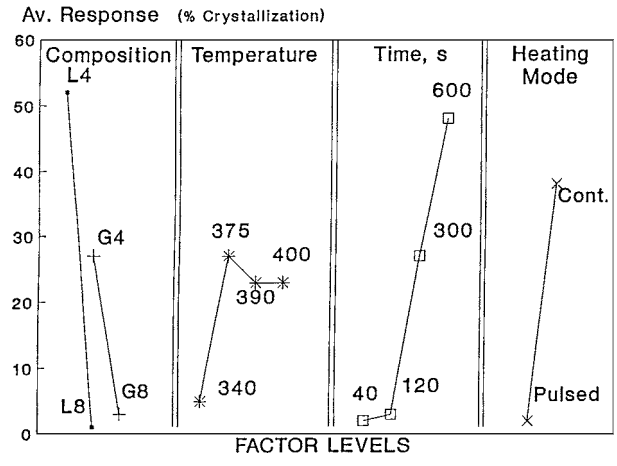

Figure 14 Factor effects of (a) composition, (b) temperature in °C, (c) time in seconds, and (d) mode of heating on the crystallization in HMF glasses during T-33 ground experiments.

samples and then saturated with a slight decrease. These results were also supported by the DTA data presented in Table II, which indicated that the onset of crystallization in these glasses was around 350°C, while most of the crystallization peaked in the temperature range of 368–388°C for all the samples, as given by crystallization peaks 1 and 2.

However, the most significant findings of these ground-based experiments are shown in Fig. 14c and d. These results indicated that a continuous heating for more than two minutes was required at appropriate temperatures to obtain a significant amount of crystallization in HMF glasses. These findings ruled out the utility of further HMF glass processing experiments on the T-33 aircraft and established the need for longer duration experiments on the sounding rocket, space shuttle or space station.

5. Conclusions

HMF glass processing experiments, conducted onboard the T-33 parabolic flight aircraft to study the effect of gravity on crystallization in these glasses, have indicated that gravity enhances crystallization in HMF glasses. These results imply that microgravity could help in reducing crystallization and resulting optical degradation during the processing of HMF glass fibres, which could lead to the predicted ultra-low losses in these fibres.

Though promising, these results cannot be considered conclusive due to the short processing time of 20 seconds on the parabolic flight aircraft. Longer duration experiments in microgravity are needed to establish the role of gravity on crystallization in HMF glasses. Our experiments have also indicated that a continuous heating of more than two minutes should be used for further crystallization studies in HMF glasses. This suggests that further experiments should be conducted on the sounding rockets, space shuttle or space station. Such experiments have indeed been conducted on the CSAR-I and CSAR-II sounding rockets and these results will be discussed in other papers.

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