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FINAL REPORT

FOR
MEA/A-1 EXPERIMENT 81F01

CONDUCTED ON STS-7 FLIGHT, JUNE 1983

CONTRACT NAS 8-34758
CONTAINERLESS PROCESSING OF GLASS FORMING MELTS

Prepared for

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, AL 35812

Prepared by

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SUMMARY

This report describes the pertinent portions of experiment 81F01 for the project "Containerless Processing of Glass Forming Melts in Space", NASA Contract NAS 8-34758. The experiment was conducted on June 19, 1983 in MEA/A-1 on the space shuttle flight STS-7 which was launched on June 18, 1983 from Cape Canaveral, Florida. The shuttle landed on June 25, 1983 at Edwards Air Force Base, California.

The rationale for the processing of glass in space, with special emphasis on the objectives of the present investigation, is described in the introduction. The procedure for preparing the precursor samples used for the flight experiment is also described briefly.

In this flight experiment, it was intended that five spherical samples (∿6 mm in diameter) of glass forming compositions would be heated, melted, and quenched in a single axis acoustic levitator/furnace designed and fabricated by Intersonics, Inc. In addition, three other non-melting samples made from alumina (Al_2O_3) were used to check the operation of the acoustic levitator/furnace under actual flight conditions. The flight hardware consisted of a furnace chamber heated with four silicon carbide heating elements, a single axis acoustic levitator for holding the sample at a fixed position in the furnace, a sample insertion (into the furnace) and retrieval mechanism, and a copper shroud for quenching the sample. A motion picture camera photographed the sample while it was being processed in the furnace.

The data stored in the flight recorder showed that six out of the eight samples were successfully inserted into and removed from the furnace. However, none of the sample attained the desired temperature. No change in weight, color, physical appearance, or shape was found for any of the flight* samples,

compared to their precursor,* except for the 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol% hot pressed sample. This flight sample had partially melted and was stuck to the platinum cage wires. A large pore ∿3 mm in diameter was found inside the flight sample. This large pore is believed to have formed from the coalescence of many much smaller pores initially present in the hot pressed precursor. The motion picture camera failed to operate properly so no photographic evidence was obtained for the behavior of the samples inside the acoustic levitator/furnace.

Because of the equipment malfunctions, none of the scientific objectives for experiment 81F01 were attained in the MEA/A-1 experiment. Nevertheless, the knowledge and experience gained from this experiment will be of value in the planning and execution of future flight experiments.

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*Precursor is used to denote the sample as prepared on earth while the term "flight" sample is used to denote a sample after flown in micro-g and returned to earth.

I. INTRODUCTION

A. Rationale for Processing Glass in Space

Glass melting in microgravity has several advantages compared to melting on earth,(1-6) namely; (a) no container is necessary to hold the melt, and (b) the reduction (or absence) of convection and density driven segregation in fluid melts. On earth, heterogeneous nucleation/crystallization commonly occurs at the melt/container interface, and this can prevent potentially interesting compositions from forming glass. This unwanted crystallization may be avoided or at least minimized by containerless processing, thereby extending the compositional region for glass formation. Limited evidence of this possibility is provided by a recent experiment in micro-g on Ge-Sb-S glasses.(7) Because of the smaller number of nuclei they contained, glasses made in micro-g were reported to be more resistant to bulk crystallization than identical samples melted on earth. Containerless melting also eliminates the chemical contamination of highly corrosive melts whose reaction with all known crucible materials cannot be prevented on earth. Thus, containerless processing offers the possibility for preparing ultrapure glasses along with glasses whose chemical composition requires temperatures above 2500-3000°C where unreactive container materials are not available. Finally, basic phenomena such as bulk diffusion,(8) chemical corrosion,(9) surface tension, bubble motion/dissolution,(10,11) etc. can be studied in fluid melts in micro-g without the disturbance of gravity-driven convection and segregation, which on earth makes the investigation of such phenomena either difficult or impossible.

B. Objectives of the STS-7, MEA/A-1 Experiment

The principal objectives of experiment 81F01 on glass melting are to:

(a) obtain quantitative evidence for the suppression of heterogeneous nucleation/crystallization in containerless melts,

(b) study melt homogenization in the absence of gravity driven convection,

(c) develop the procedures for preparing precursor samples that will yield bubble-free, high purity, chemically homogeneous melts in micro-g,

(d) perform comparative property analysis of glasses melted on earth and in micro-g, and

(e) assess the suitability of the levitator/furnace apparatus for processing multicomponent, glass forming melts in micro-g.

The compositions of the samples used in the present experiment along with their purpose is described briefly in Table I. For further details consult our Experiment Requirement and Implementation Plan (ERIP) report, dated 26 March 1982.

The suppression of heterogeneous nucleation/crystallization, the direct consequence of which is an extension of the compositional limits for glass formation, were to be studied by the containerless melting and cooling of compositions having different critical cooling rates. The critical cooling rate, R_c, is defined as the slowest rate at which a melt can be cooled without crystallizing (i.e., form a glass). If heterogeneous nucleation is absent in containerless melts in micro-g, then it should be possible to quench such melts to glass at rates less than R_c on earth where heterogeneous nucleation occurs. Thus, the ratio of R_c (earth) to R (shuttle) for melts quenched to glass in micro-g should exceed unity and the absolute value of this ratio can

Table I. Samples for STS-7, MEA/A-1 Experiment Arranged in Order of Processing.

	Sample Composition (mol%) and Description	Purpose	Time-Temperature Profile	Time (Min)	Elapsed Time (Min)
			preheat furnace to 1000°C	12	12
1	Low density (hollow) Al_2O_3 (polycrystalline solid)[3]	1. Operational check of levitator to confirm positioning and positioning stability. 2. Determine relative effects of acoustic streaming and positioning. Nonmelting sample is of comparable density to samples used on earth. 3. Confirm data from 1 g measurements.	Insert sample at 1000°C		
			Hold at 1000°C	1	
			Heat to 1200°C	1.5	
			Hold at 1200°C	1	
			Passive cooling (no shroud) to 1000°C	1	
			Retrieve sample		16.5
			preheat furnace to 1000°C	1	17.5
2	High density Al_2O_3 (polycrystalline solid)	Operational check of levitator for items 1, 2, and 3 above, but using sample whose higher density approaches that of glass forming melts.	Insert sample at 1000°C		
			Hold at 1000°C	1	
			Heat to 1200°C	1.5	
			Hold at 1200°C	1	
			Heat to 1400°C	3	
			Insert cooling shroud		
			Cool to 1000°C	2	
			Retrieve sample		27
			preheat furnace to 1000°C	1	28
3	39.3 Ga_2O_3-35.7 CaO-25 SiO_2 hot pressed containing large (∼100-150 μm) SiO_2 particles	1. Operational check of levitator for liquid sample. 2. Evaluate improvement in homogeneity. 3. Assess precursor preparation procedures. 4. Specimen for comparative property analysis with terrestrial sample. R_c = 4-6°C/s	Insert sample at 1000°C		
			Heat to 1200°C	2	
			Hold at 1200°C	1	
			Heat to 1500°C	6	
			Hold at 1500°C	4	
			Insert cooling shroud		
			Cool to 700°C	3	
			Retrieve sample		44

Table I (cont'd)

			preheat furnace to 1500°C	12	56
4	39.3 Ga_2O_3-35.7 CaO-25 SiO_2 glass (devitrified) containing colored droplet on external surface	1. Operational check of levitator for liquid sample. 2. Determine extent of mixing in melt. 3. Assess precursor preparation procedures. 4. Acquire evidence of temperature gradients in melt.	Insert sample at 1500°C		
			Hold at 1500°C	2	
			Insert cooling shroud		
			Cool to 700°C	3	
			Retrieve sample		61
			preheat furnace to 1500°C	12	73
5	56 Ga_2O_3-44 CaO, glass (devitrified)	1. Operational check of levitator with sample that is initially solid, but melts at 1323°C. 2. Determination of enhanced glass formation. $R_c \approx 550°C/s$ 3. Specimen for comparative property analysis with terrestrially prepared samples.	Insert sample at 1500°C		
			Hold at 1500°C	4	
			Insert cooling shroud		
			Cool to 700°C	3	
			Retrieve sample		80
			Preheat furnace to 900°C max.	2	82
6	33.3 Na_2O-66.7 B_2O_3 glass containing gas bubbles	1. Acquire data for bubble behavior (movement, dissolution/growth, nucleation, coalescence). 2. Assess melt rotation.	Insert sample at 900°C		
			Hold at 900°C	5	
			Insert cooling shroud		
			Cool to 400°C	12	
			Retrieve sample		99
			Preheat furnace to 1350°C max.	8	107
7	45 Na_2O-55 SiO_2, glass (devitrified)	1. Determination of enhanced glass formation. $R_c \approx 2$-$3°C/s$ 2. Specimen for comparative property analysis with terrestrial glass sample.	Insert sample at 1350°C		
			Hold at 1350°C	5	
			Insert cooling shroud		
			Cool to 500°C	5	
			Retrieve sample		117

Table I (cont'd)

			preheat furnace to 1550°C	10	127
8	High density Al_2O_3, same as sample 2. (polycrystalline solid)	1. Operational check of levitator at maximum design temperature. 2. Test insertion apparatus at maximum temperature.	Insert sample at 1550°C		
			Hold at 1550°C	3	
			Insert cooling shroud		
			Cool to 1000°C	3	
			Retrieve sample		133

be used as a quantitative measure of the degree to which the glass formation is enhanced, or conversely, heterogeneous nucleation is suppressed in containerless melts. This was the purpose of the samples 5 and 7 in Table I, whose R_c on earth is from ∿30 to ∿5 times higher, respectively, then the cooling rate of the furnace used in micro-g.

Melt homogenization in the convection-free environment of micro-g will be investigated also by observing the level of homogeneity achieved from precursor samples made with known chemical and optical inhomogeneities. Sample 4, which contains a colored droplet on its external surface, and sample 3, which is an inhomogeneous hot pressed sample containing relatively large SiO_2 particles (100 to 300 μm) were used for this purpose. A wide range of physical, optical, thermal, and mechanical properties will be measured for glasses made in micro-g and compared with the same properties measured for glasses made on earth. The purpose of the sodium-borate sample (#6) is to provide information for the behavior of gas bubbles and supplemental data for melt homogenization in micro-g.

There was no special basis for selecting the different sample compositions for this experiment. The ternary gallia-calcia-silica composition (samples 3 and 4) was chosen primarily because of its prior use in two glass melting experiments in space, SPAR VI(12) and VIII.(13) The sodium-silicate system had been thoroughly studied and the 45 mol% Na_2O composition had a desirable R_c value. The binary gallia-calcia composition (sample 5) has a very high critical cooling rate (∿550°C/s) and, at one time, was felt to have potentially interesting optical properties.

An important practical objective of the experiment was to determine the suitability of using hot pressed, precursor samples for containerless melting. Precursor samples made by sintering/hot pressing have the advantage of being easily prepared without contamination from a container. Thus, it was of interest to determine the degree of chemically inhomogeneity that can be tolerated in a hot pressed, precursor, but which will yield a chemically homogeneous multicomponent melt in a reasonable time in micro-g.

II. PREPARATION OF PRECURSOR SAMPLES

The preparation procedures for samples 3, 4, 5, and 7 are described since they were the only samples prepared at UM-Rolla. The alumina samples 1, 2, and 8, used primarily for an engineering checkout of the levitator/furnace, were supplied by Intersonics, sample 6 was prepared by Prof. S. Subramanian of Clarkson College, NY.

Sample 3 was a hot pressed 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol% composition. The appropriate proportions of Ga_2O_3 (electronic grade, purity 99.999%)* and $CaCO_3$ (reagent grade) were first wet mixed (alcohol). After drying, -50 to +140 mesh size vitreous silica (purity 99.99%)** was added and the dry batch tumbled for ∿5 h. The powdered batch was cold pressed in a graphite mold at 2000 psi for 5 min and then hot pressed at 1000°C and 1000 psi for ∿6 h in an argon gas atmosphere. The hot pressed material was left inside the graphite mold and cooled slowly. The flow of argon gas was continued during cooling. After removing the hot pressed cylinder (3.81 cm diameter and 2.52 cm long) from the press, it was heated at 1000°C for ∿5 h to burn out any carbon on its outer surface. To avoid contamination, the outer surface of the hot pressed cylinder which contacted the graphite mold was discarded and spherical samples

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*Eagle-Picher Industries

**GEM-435 Fused Quartz, Engineered Materials

∿6 mm diameter were ground by hand from the center of the hot pressed cylinder. The spherical samples were cleaned with acetone in an ultrasonic cleaner, heated to ∿950°C for ∿12 h and then stored in a vacuum desiccator.

Sample 4 was made from a 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol% glass which was melted in a platinum crucible at ∿1500°C. The melt was stirred with a silica rod 5 times every 15 min to ensure good homogenization. After the final stirring, the melt was held in the furnace (at 1500°C) for another 30 min. The furnace temperature was then lowered to 1450°C and the melt held at this temperature for 1 h. The melt was then cast into a preheated (500°C) graphite mold having four spherical (∿8 mm diameter) cavities. A loaf casting (rectangular bar) was also made from the same melt and this glass was used for property measurements. After cutting off the casting stem, the glass spheres were annealed at 500°C and cleaned with acetone. Previously prepared droplets (∿1 to 2 mm diameter) of the same overall composition, but colored with 3 wt% CoO, were fused onto each sphere using a spot heater. The colored droplets were prepared by melting the CoO-containing glass in the same way as described above and then pouring the melt onto a clean stainless steel plate from a height of ∿4 ft. Numerous small spheres ≤ 2 mm diameter were formed. The spheres with the colored drop fused on their surface were cleaned with acetone in ultrasonic cleaner, devitrified by heating at 1000°C for one hour and stored in a vacuum desiccator.

To prepare sample 5, a 56 Ga_2O_3-44 CaO, mol% glass was melted in a platinum crucible at 1500°C for 45 min and stirred several times with a silica rod. This is a fluid melt at 1500°C with an estimated viscosity of < 10 poise. Before casting, the melt temperature was lowered to 1450°C and the melt was then cast into water at 27°C. The roughly spherical glass pieces obtained by water quenching were annealed at 700°C, cooled to room temperature, cleaned with acetone in an ultrasonic cleaner, and then stored in a vacuum desiccator.

The 45 Na_2O-55 SiO_2, mol% glass (sample 7) was prepared by melting in a platinum crucible at 1400°C. Glass spheres ∿8 mm diameter were made by pressing the glass in a graphite mold, the same procedure as used for sample 4. The spheres were annealed at 400°C, devitrified at 750°C for one hour, and were stored in de-aired mineral oil.

Before sending these precursor samples to the Marshall Space Flight Center (MSFC), they were photographed from three orthogonal directions, weighed, and their dimensions measured. They were then sealed in evacuated (40-50 μm pressure) glass tubes. Figures 1 through 4 are photographs of the precursors used for the MEA/A-1 experiment, STS-7. The weights, dimensions, and density for each precursor are recorded in Table II. Precautions were taken to avoid any contamination when handling each sample. The details of the pre- and post-flight sample handling procedure are given in our Sample Handling and Analysis Plan (SHAP) report, dated April 1982.

The precursor samples were hand carried to MSFC. The glass vial containing the primary precursor sample was broken and the weight of each precursor was measured in a dry box filled with dry argon. As shown by the weights in Table III, there had been no detectable change in weight for any precursor during storage. After weighing, the precursor samples were installed in their respective injection cages, again in a drybox filled with dry argon. The injection cages were then installed in the levitator/furnace apparatus which was part of the MEA/A-1 equipment package. This installation was done in a plastic tent to minimize exposure to the water vapor in the ambient atmosphere.

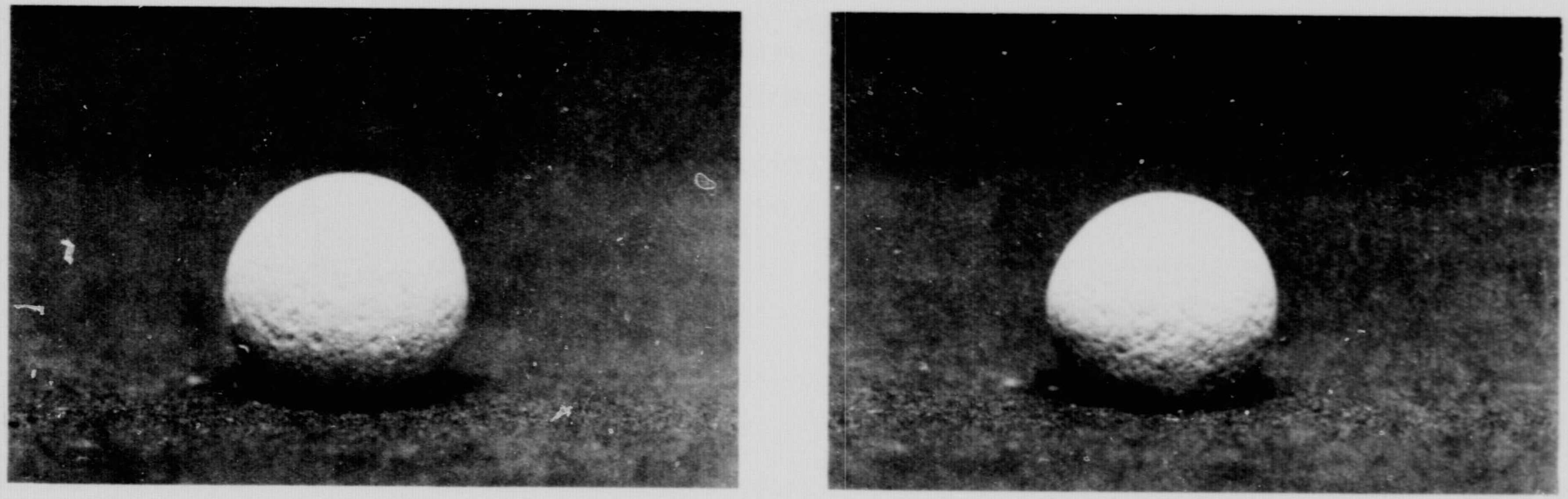


Figure 1. 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol%, hot pressed precursor sample (#3) used in MEA/A-1, STS-7.

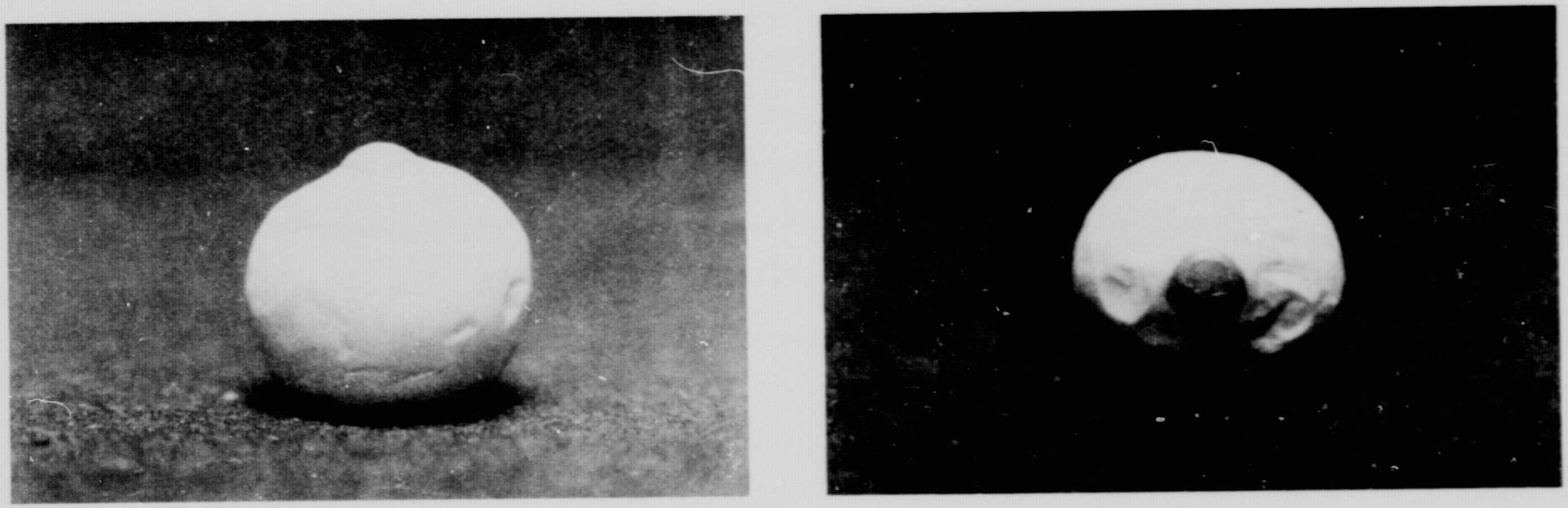


Figure 2. 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol%, devitrified glass sample with colored spot (#4) used in MEA/A-1, STS-7.

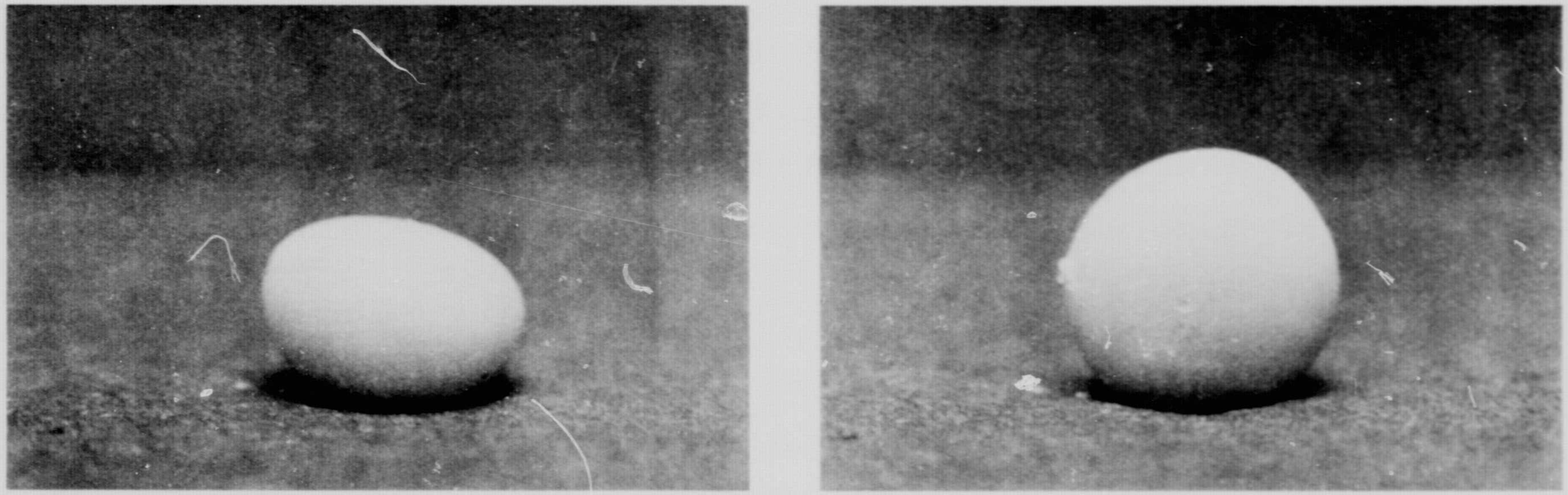


Figure 3. 56 Ga_2O_3-44 CaO, mol% devitrified glass sample (#5) used in MEA/ A-1, STS-7.

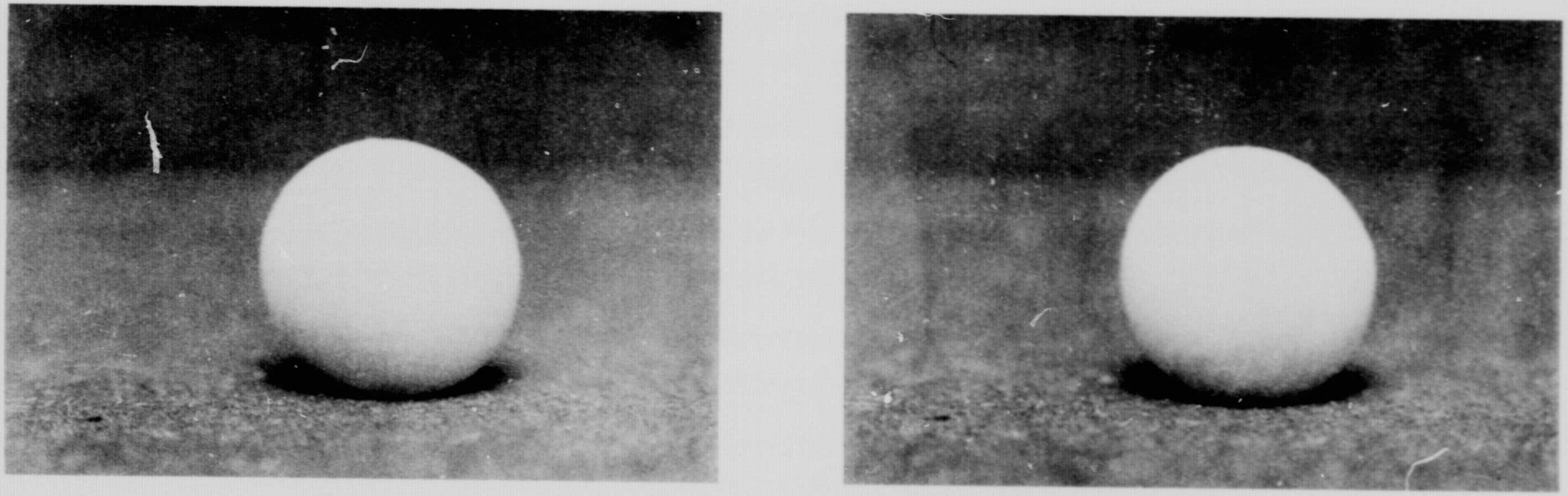


Figure 4. 45 Na_2O-55 SiO_2, mol% devitrified glass sample (#7) used in MEA/A-1, STS-7.

Table II. Initial Weight, Diameter, and Density of Precursor Samples, Measured at UMR at Time of Sealing in Glass Vials.

	Sample Composition,* in mol%	Weight (gms) $\pm$ 0.00005	Average Diameter (cm)	Density (gms/cm^3) $\pm$ 0.015
#3	39.3 Ga_2O_3-35.7 CaO-25 SiO_2 hot pressed, measured open porosity was ∿10%	0.60560	0.705 ± 0.005	3.466
#4	39.3 Ga_2O_3-35.7 CaO-25 SiO_2 glass (devitrified) with blue dot	1.05150	0.777 ± 0.040	4.316
#5	56 Ga_2O_3-44 CaO glass (devitrified)	0.76600	a) 0.766 ± 0.015 b) 0.573 ± 0.025 ($a \perp b$)	4.430
#6	33.3 Na_2O-66.7 B_2O_3 glass containing air bubbles**	0.16699	0.504 ± 0.030	2.347
#7	45 Na_2O-55 SiO_2 glass (devitrified)	0.69970	0.820 ± 0.026	2.536

*Samples #1, #2, and #8 were not measured.

**Measured at Clarkson College, NY.

Table III. Weight of Precursor Samples.

Sample Number	Weight (gms) measured at UMR, Aug. 28, 1982*	Weight (gms) measured at MSFC, Jan. 25, 1983**	Difference in weight (gms)
3	0.60560	0.60342	- 0.00218
4	1.05150	1.05069	- 0.00081
5	0.76600	0.76526	- 0.00074
6	0.16699[a)]	0.16551	- 0.00148
7	0.69970	0.70245	+ 0.00275
1 gm standard weight	1.00020	0.99957	- 0.00063

*At time of sealing in glass vials.

**At time of installation in acoustic levitator/furnace.

[a)] Measured at Clarkson College, NY on July 19, 1982.

III. PROPERTY ANALYSIS OF TERRESTRIALLY PREPARED SAMPLES

A sizeable quantity of the same material from which the precursor sample was prepared, was saved for measuring different physical, thermal, and optical properties which were to be compared with the properties of the flight sample. The properties evaluated for the 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, 56 Ga_2O_3-44 CaO and 45 Na_2O-55 SiO_2, mol% glasses are listed in Table IV. The inhomogeneities present in the hot pressed 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol% precursor were studied by examining a fracture surface with scanning electron microscopy (SEM). Figures 5 and 6 show the presence of numerous pores, Ga_2O_3 rich phases of large size and unreacted silica particles. X-ray diffraction (XRD) analysis of the hot pressed precursor established the presence of β-Ga_2O_3, $CaGa_2O_4$, and small amount of $Ca_2Ga_2SiO_7$ (Table IX). The unreacted silica particles were not detected by XRD since vitreous silica was used in the batch. A small sample of this hot pressed material yielded a good homogeneous glass as examined by SEM when it was given the thermal treatment planned for the flight experiment, i.e., at 1500°C for 4 min (see Table I for sample 3).

IV. POST-FLIGHT SAMPLE REMOVAL, HANDLING, AND FLIGHT EVENTS

The MEA/A-1 flight apparatus was returned to MSFC, Huntsville, AL on July 8, 1983. It was covered with a plastic tent in a large dust free room and was opened on July 13, 1983. The sample injectors were removed from the carousel assembly in the acoustic levitator/furnace in the sequence sample number 6-7-3-4-5-8-1-2. Each injector was placed in a plastic container which was purged with dry air before sealing. One packet of silica gel desiccant was placed in each plastic container except for those containing the alumina

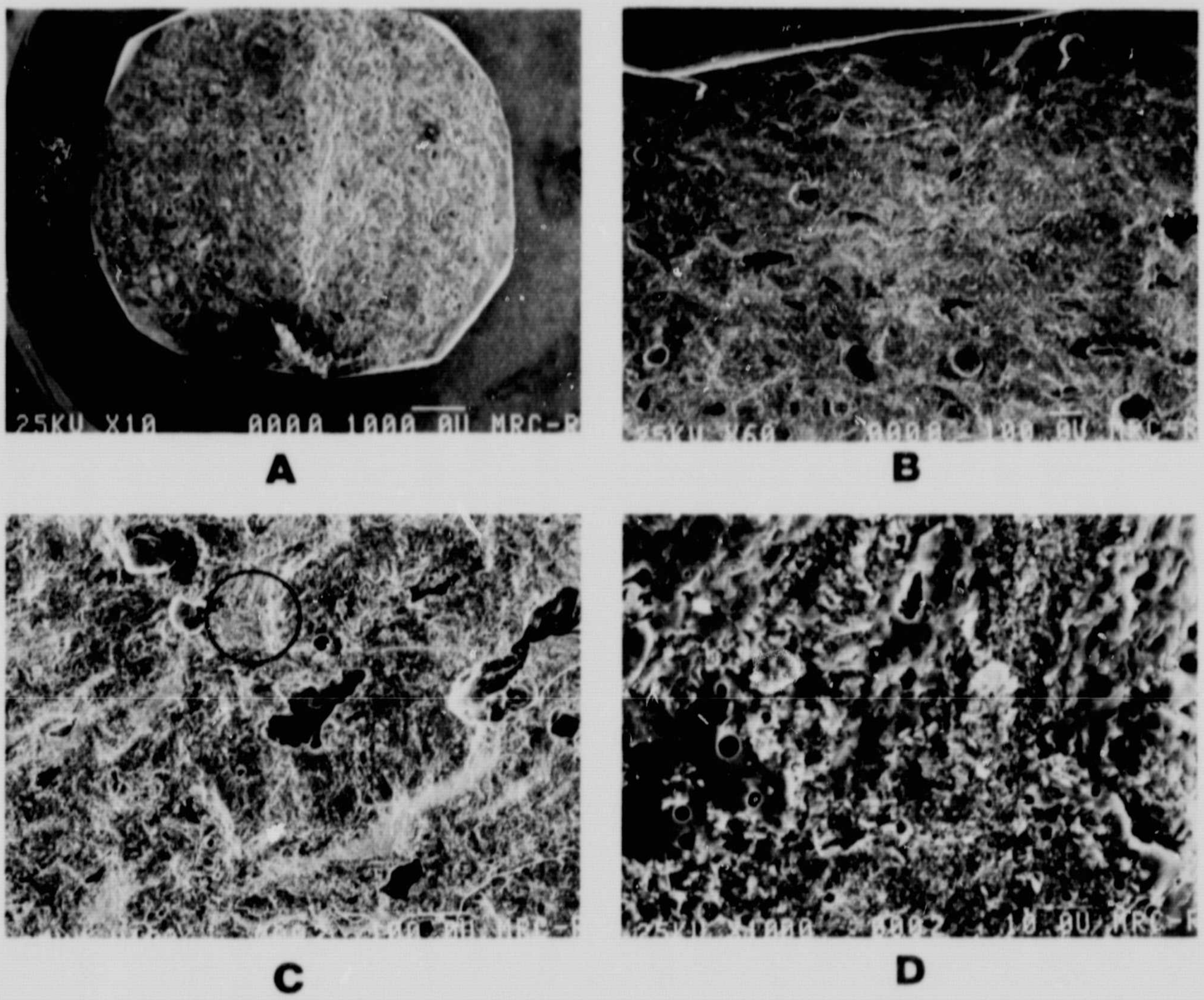


Figure 5. Appearance of the interior of the hot pressed 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol%, precursor sample as seen by SEM. A: overall view of fracture surface, black spots are the voids; B,C: magnified views of the voids (dark regions); D: magnified view of the region circled in C.

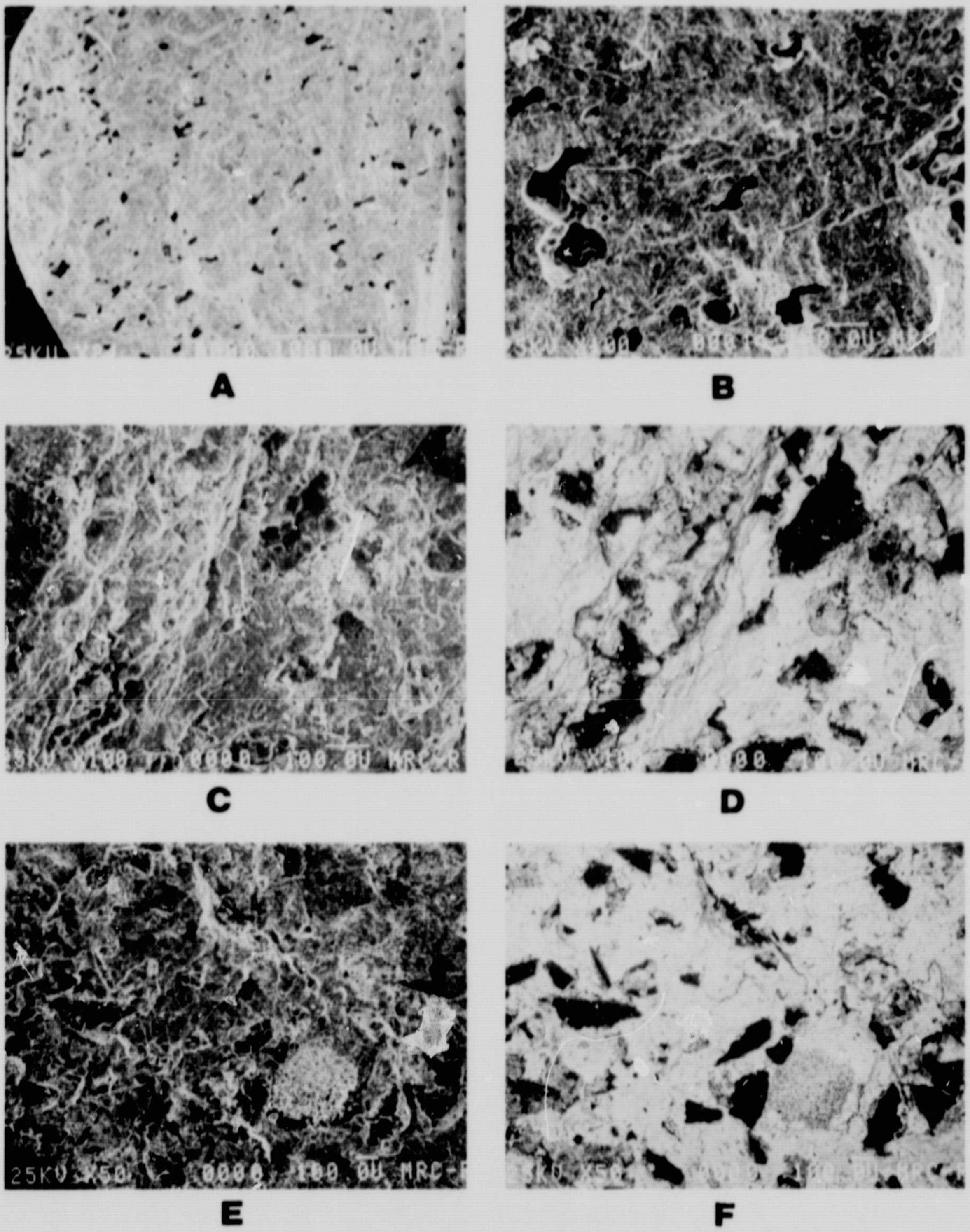


Figure 6. Fracture surface of the hot pressed 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol%, precursor sample. A: overall view, B: voids (dark regions), and C to F: different crystalline phases. D and F are back scattered electron spectra of the same regions shown in C and E, respectively. Darker regions in D and F are silica particles, white regions are rich in Ga_2O_3 and gray regions are $Ca_2Ga_2SiO_7$.

Table IV. Properties of Terrestrially Prepared Glasses.

	56 Ga_2O_3-44 CaO*	39.3 Ga_2O_3-35.7 CaO-25 SiO_2*	45 Na_2O-55 SiO_2*
Precursor Sample No. (Table I) of equivalent composition	5	3 and 4	7
Density, D (g/cm^3)	4.48 ± 0.015	4.195 ± 0.015	2.423 ± 0.015
Critical Cooling Rate, R_c (°C/s)	550 ± 50	4 ± 2	2 ± 1
Crystallization Temp. T_x (°C)	775 ± 5	940 ± 5	600 ± 5
Refractive Index, η_D	1.7985 ± 0.0008	1.7121 ± 0.0008	1.509 ± 0.0008
Dispersion, $\eta_F-\eta_C$	0.0290 ± 0.0015	0.0175 ± 0.0015	0.0140 ± 0.0015
Abbe Number, ν	27.4 ± 2.5	40.5 ± 2.5	36.4 ± 2.5

*Compositions are in mol%.

samples, injectors 1, 2, and 8. The containers were then taken to a glove box filled with dry argon (measured relative humidity < 13% at ∿25°C), where the flight samples were removed from their injector assembly. The flight samples were handled inside the drybox with a vacuum chuck (manipulator). The hot pressed/sintered calcia-gallia-silica sample in injector 3 could not be removed since it had partially melted and was stuck to the platinum wire cage. The other flight samples were weighed (excluding #1, 2, 3, and 8) inside the drybox, photographed, and sealed (except #3) in evacuated glass tubes and hand carried to the University of Missouri-Rolla (UMR). Cage 3, to which sample 3 was attached (Fig. 7), was carried inside a plastic bag containing desiccants.

In this report only those aspects of the performance of the acoustic levitator/furnace hardware which are pertinent to our experiment are described. Visual observation of the flight samples, just after their removal from the MEA/A-1 assembly, indicated no apparent change in their color, shape, and surface condition, except for sample 3 which was stuck to the platinum wire cage. The visual observations are summarized in Table V. The platinum wire cage of sample 3 was blackened considerably. The copper cooling shroud was also discolored. Some black flakes were found near the cooling shroud gate of the acoustic levitator/furnace. From the "Quick Look Report" submitted to NASA by Intersonics (July, 1983) it was stated that the levitator/furnace did not function properly during this flight experiment because of inadequate cooling which lead to an overheating of the electronic components. The cooling shroud did not retract fully during the processing of the third sample and the cooling shroud gate remained open. This caused a larger than expected heat loss from the furnace and aggravated the overheating problem. The computer controls, therefore, shut the furnace off after the fourth sample and the entire system was turned off after the sixth sample. The

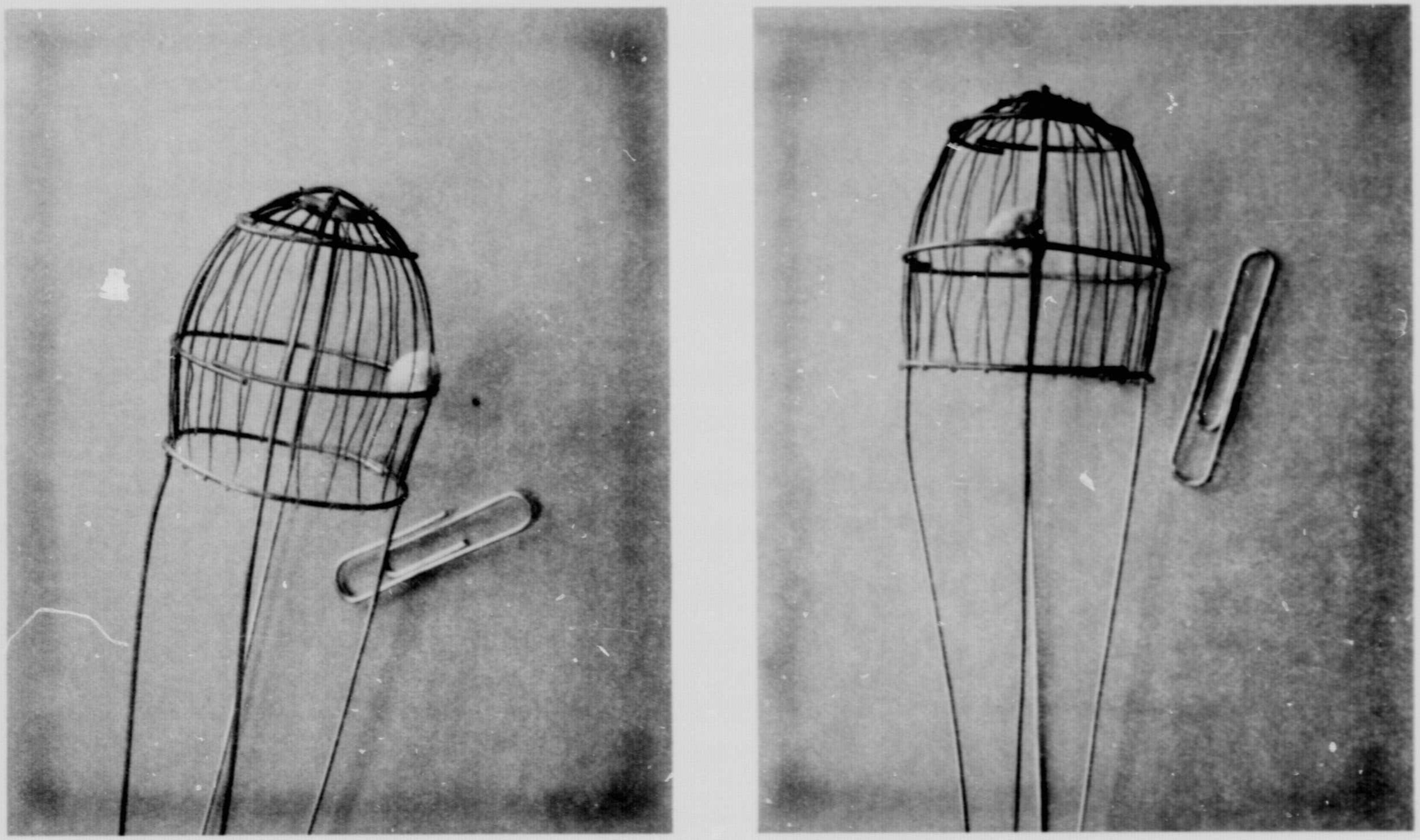


Figure 7. Flight sample 3 (39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol%, hot pressed) stuck to platinum wire cage. Paper clip is used for dimensional scale.

Table V. Visual Observation of Flight Samples.

Sample Number and Processing Order	Sample Position in Cage	Change in Shape and/or Color
1. Low density alumina	Inside cage, but displaced slightly to one side	None
2. High density alumina	At center of the cage	None
3. Calcia-Gallia-Silica* hot pressed	Stuck to wire cage	No change in white color, sample deformed, surface smoother than for precursor, wire cage blackened
4. Calcia-Gallia-Silica* with blue spot	Inside cage, but displaced slightly to one side	None
5. Calcia-Gallia**	At center of the cage	None
6. Borax with gas bubbles	At center of the cage	None, bubble positions unchanged
7. Soda-Silica (45 Na_2O-55 SiO_2)	Center of the cage, but was not released for levitation	None
8. High density alumina	Center of the cage, but was not released for levitation	None

*35.7 CaO-39.3 Ga_2O_3-25 SiO_2, mol%

**56 Ga_2O_3-44 CaO, mol%

flight recorder data indicate that samples 1 through 6 were successfully inserted into and retrieved from the furnace, but none of the samples attained the temperature specified for the flight experiment. The maximum temperature actually attained for each sample is compared with the desired temperature in Table VI. The motion picture camera used to record the behavior of the levitated samples inside the furnace also malfunctioned and the entire film was unexposed. Thus, no photographic evidence of the flight samples was obtained. The atmosphere in the MEA/A-1 apparatus holding the acoustic levitator/furnace hardware was dry (missile grade) air.

V. ANALYSIS OF FLIGHT SAMPLES

A. Weight

As mentioned previously, there was no change in the color, dimensions, and surface condition of the flight samples as compared to their precursor except for sample 3 which was stuck to the cage wire. The post-flight analysis was conducted, therefore, only on sample 3. The pre- and post-flight weight of samples number 4, 5, 6, and 7 are compared in Table VII. The slight weight gain for each sample, which is essentially the same as that for the standard weight, is attributed to the weighing procedures and to the balance used. The weight of the samples is concluded to have remained constant.

B. General SEM Examination

The black flakes found near the cooling shroud gate were analyzed by SEM and are shown in Fig. 8. These flakes contained copper, zinc, and tin. SEM analysis of the blackened Pt-Rh wire from cage 3 again showed copper to be the major impurity. The external surface of the flight samples examined by SEM was also found to be contaminated by some unwanted elements including copper,

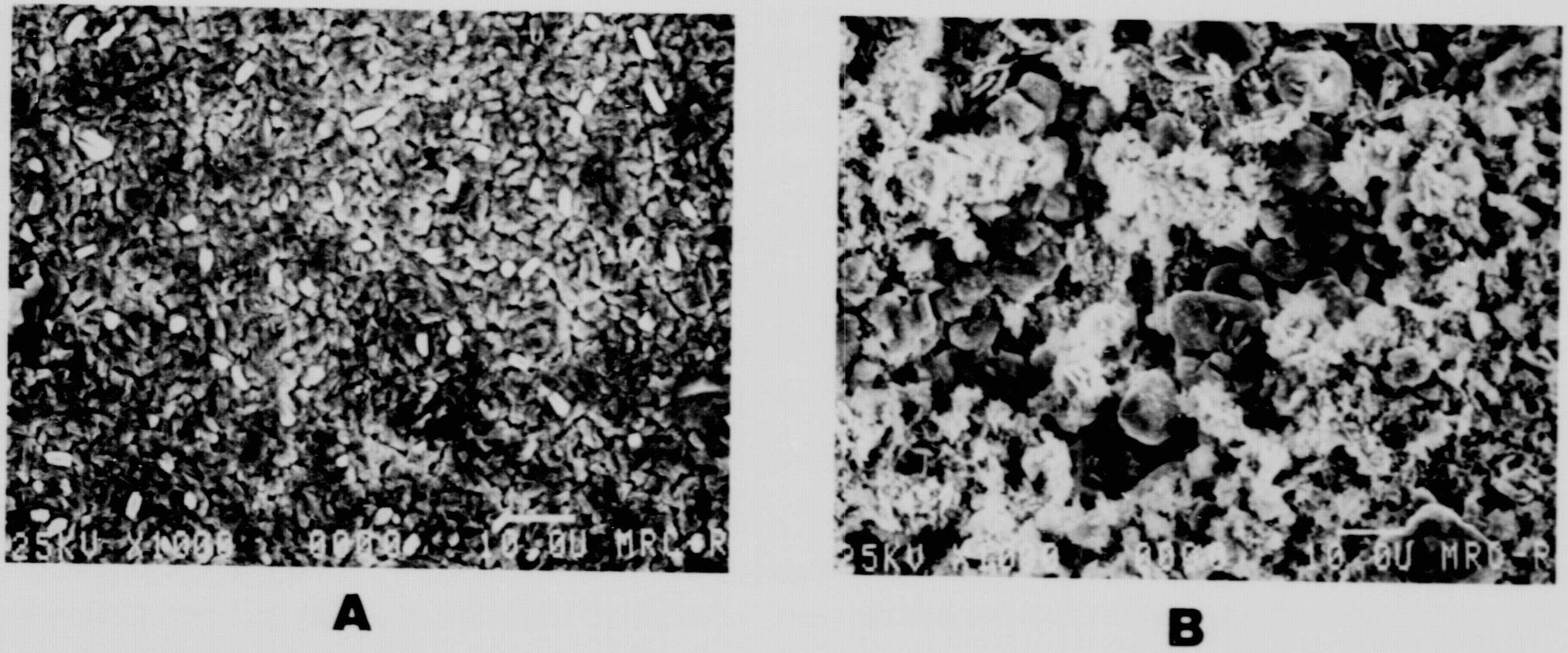


Figure 8. SEM of the black flakes found near the cooling shroud gate of the acoustic levitator/furnace when it was opened at MSFC after the flight experiment. The material mainly consists of Cu, Zn, and Sn, probably as oxides. The white regions are essentially copper (oxide).

Table VI. Maximum Temperature Planned and Attained in MEA/A-1 Flight Experiment.

Sample Number	Maximum Temp. (°C) Planned	Actual	Remarks
1	1200	1170	Inserted/retrieved
2	1400	1340	Inserted/retrieved
3	1500	1439	Sample stuck to the cage
4	1500	1220	Inserted/retrieved
5	1500	597	Inserted/retrieved
6	900	435	Inserted/retrieved
7	1350	Samples not inserted as the mechanism did not work.	
8	1550		

Table VII. Weight of Precursor and Flight Samples, MEA/A-1 Experiment.

Sample No.	Weight (gms) of Precursor* (± 0.00005)	Weight (gms) of Flight Sample** (± 0.00005)	Difference (gms)
4	1.05069	1.05176	+ 0.00107
5	0.76526	0.76620	+ 0.00094
6	0.16551	0.16660	+ 0.00109
7	0.70245	0.70408	+ 0.00163
1 gm standard weight	0.99957	1.00058	+ 0.00101

*Measured at MSFC on 1/25/83.

**Measured at MSFC on 7/13/83.

see Table VIII. The fracture surface of sample 3 did not show any evidence of contamination in the bulk of this specimen. The source of the different impurities on the external surface of these samples and the black flakes near the cooling shroud gate is not known with absolute certainty. However, the most likely source of copper contamination and discoloration of cage 3 is the overheated copper cooling shroud which remained partially inside the furnace during the cooling of sample 3.

C. Detailed Examination of Sample 3

Sample 3, which was the hot pressed 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol%, was returned stuck to the cage wires (see Fig. 7) and was a partially crystalline solid. As mentioned earlier, this sample was not processed according to the planned flight schedule (see Table I for sample 3). The maximum temperature in MEA/A-1 for this sample was briefly ∿1440°C instead of the planned 1500°C (Table VI). Upon reaching 1440°C, the temperature started decreasing and was above 1400°C for only 1.5 min. A ground based experiment conducted at UMR consisted of heating a sample of the same hot pressed material using the same time-temperature schedule that was recorded for sample 3 in the MEA/A-1 flight experiment. This sample was partially melted and crystallized on quenching to room temperature. Thus, the appearance of flight sample 3 is consistent with its thermal treatment (time/temperature) as recorded in MEA/A-1. XRD analysis of flight sample 3 showed that it contained three crystalline phases, $Ca_2Ga_2SiO_7$, β-Ga_2O_3, and α-Ca_3SiO_7. These phases and the XRD pattern closely resembled those for a 35.7 CaO-39.3 Ga_2O_3-25 SiO_2, mol% glass devitrified at 1000°C for 1 h (Table IX). The crystalline phases present in the hot pressed precursor were mostly β-Ga_2O_3 and $CaGa_2O_4$ with a small amount of $Ca_2Ga_2SiO_7$.

Table VIII. Impurities Detected by EDAX on MEA/A-1, STS-7 Flight Samples.

Sample No.	Surface Analyzed	Impurities Detected Major	Impurities Detected Trace
1	External	Si	None
2	External	Si,Pt	None
3	External	Cu	Fe,Ti
3	Fracture	None	None
4	External	Al,S,Pt,Rh	None
8	External	Si	S,Cu,Zn
Pt-Rh wire from Cage 3	External	Cu,Al,Si	Fe,Zn,Ca
Alumina spaghetti from Cage 3	External	Cu	Fe
Black flakes (found near the gate to cooling shroud)	---	Cu,Zn,Sn	Si,S,K

Table IX. Crystalline Phases Identified by XRD in Different Samples Prepared from 35.7 CaO-39.3 Ga_2O_3-25 SiO_2, mol% Composition.

Sample Description	Crystalline Phases Identified
Flight sample 3, processed in MEA/A-1, STS-7	β-Ga_2O_3, α-$Ca_3Si_2O_7$, and $Ca_2Ga_2SiO_7$
Glass sample devitrified at 1000°C for 1 h	β-Ga_2O_3, α-$Ca_3Si_2O_7$, and $Ca_2Ga_2SiO_7$
Hot pressed compact from which precursor 3 was made	β-Ga_2O_3, $CaGa_2O_4$, and a small amount of $Ca_2Ga_2SiO_7$

The external surface as well as the interior of flight sample 3 were examined by SEM. Figures 9 and 10 show the general appearance of the external surface. The presence of pores (holes) on the external surface is easily seen in Fig. 9. Ga_2O_3-rich crystals are also very common on the external surface (Fig. 10).

A large nearly spherical pore ∿3 mm in diameter was found inside flight sample 3 when it was broken in half, see Fig. 11. This large pore is nearest to the external surface opposite that which was attached to the platinum cage. The platinum wire to which the sample was attached would be at the top of Fig. 11A. This pore was not visible when the external surface was examined, but is within ∿150 μm of the external surface at its closest point--lower left hand corner of Fig. 11A. In addition to this large pore, the interior of this sample also contains numerous other smaller spherical pores, many being close to the external surface. These pores range from a few μm to ∿500 μm in diameter. The shape of these pores is clearly different from those irregularly shaped voids initially present in the hot pressed precursor, Figs. 5 and 6. Figure 12 shows the interior of the other half (A) of flight sample 3. Ga_2O_3 crystals are present on the walls of the pores. An enlarged view of the bulk across the fracture surface is shown in Fig. 13. Compositional analysis (EDAX) of this region in the sample did not show any evidence of unmelted silica particles that were uniformly distributed in the precursor sample (Fig. 6D and F).

The large pore shown in Figs. 11A and 12A is of particular interest since the precursor contained only much smaller pores of irregular shape. The estimated volume of this large pore, ∿0.0141 cm^3, is reasonable in terms of the measured open porosity (∿10%) initially present in the precursor which totaled ∿0.0183 cm^3. It is clear that a major fraction of the pore volume,

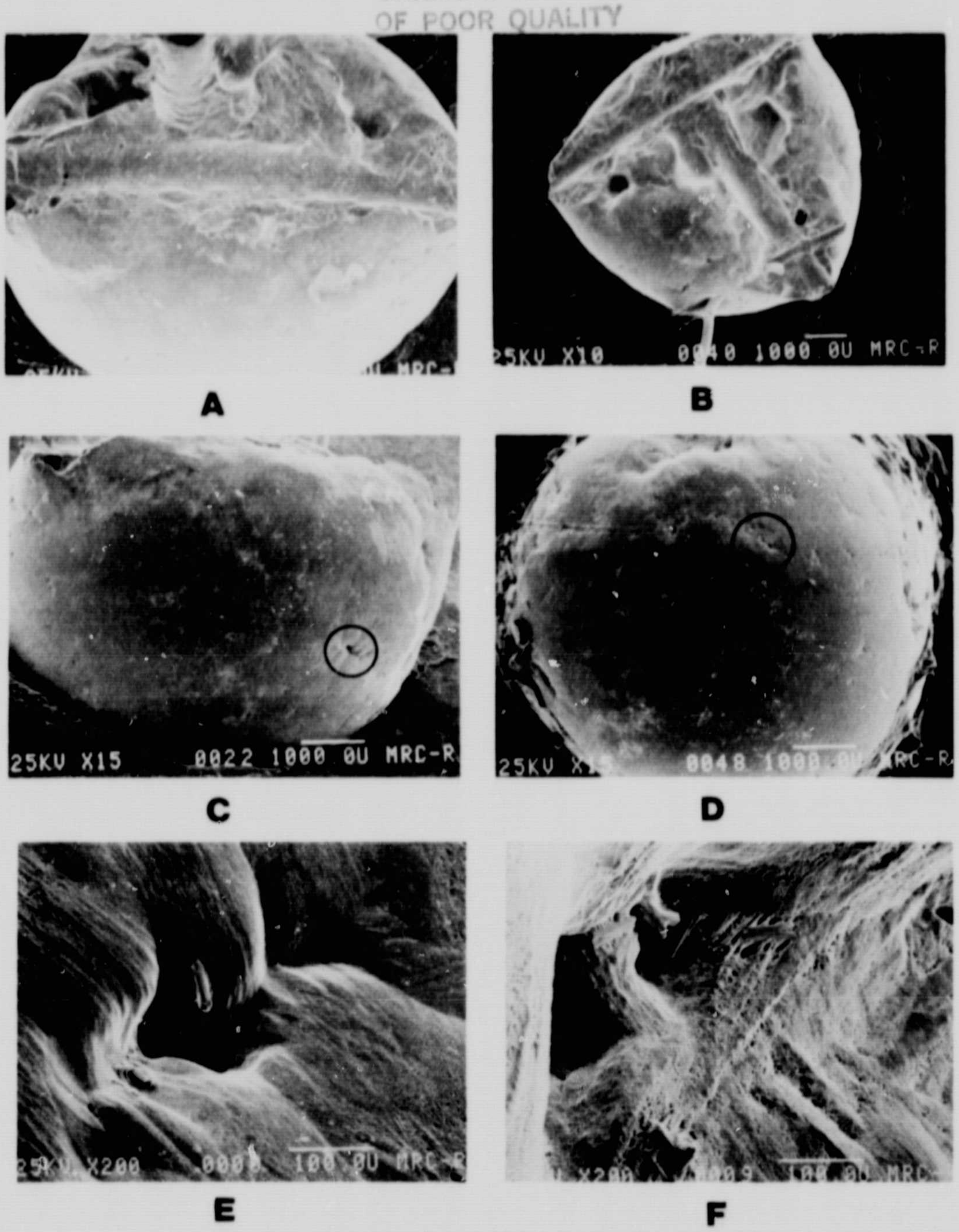


Figure 9. SEM of the external surface of the hot pressed 39.3 Ga_2O_3-35.7 CaO-25 SiO_2, mol% flight sample (#3) from MEA/A-1, STS-7 after removal from platinum wire. A to D: general appearance of the flight sample for different orientations. The impression of the cage wire to which the flight sample stuck during the flight experiment is prominent in A and B. The presence of voids (holes) at the external surface is apparent also. E and F show enlarged views of the holes circled in C and D, respectively.

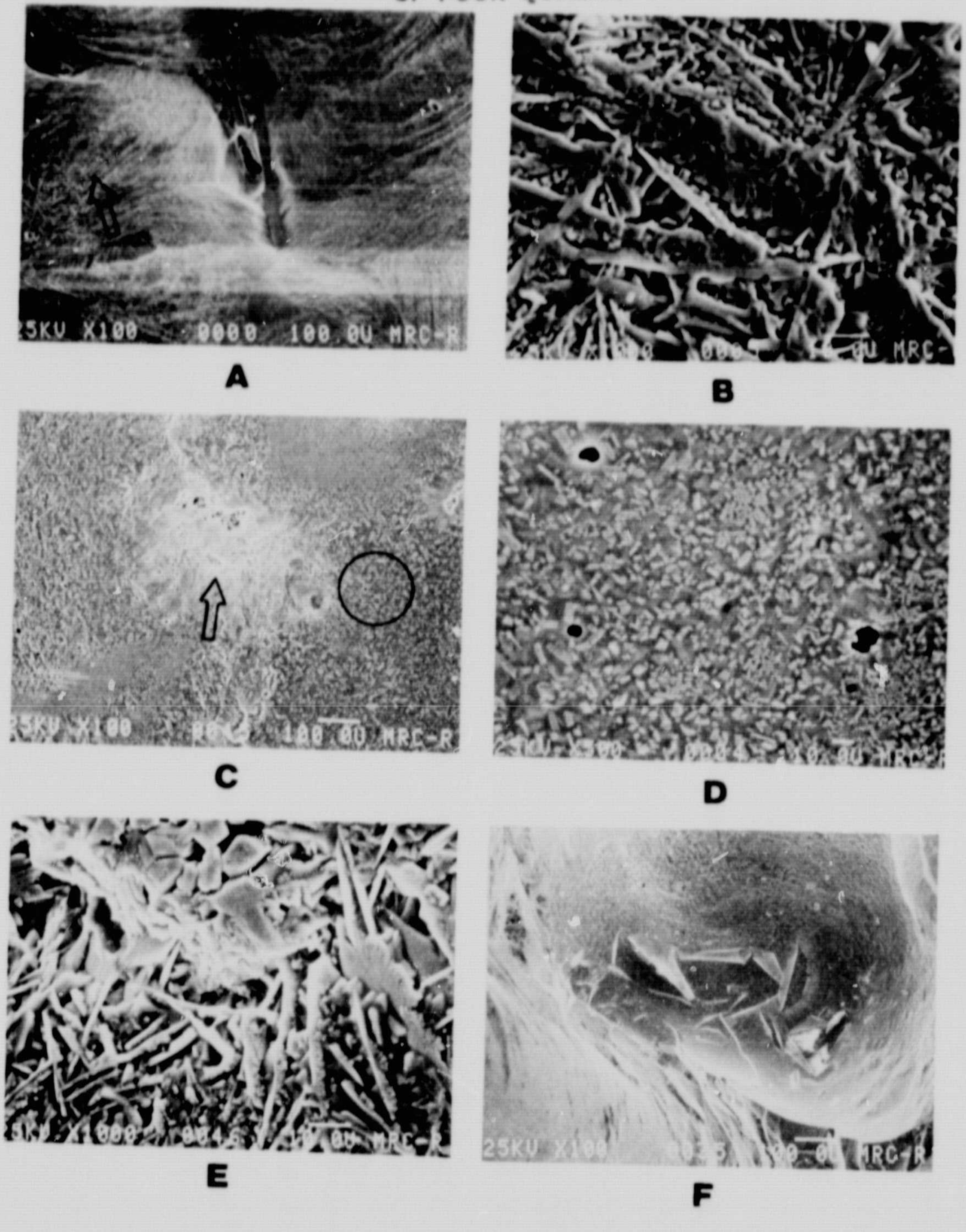


Figure 10. External surface of flight sample #3 (MEA/A-1, STS-7). A,C: different types of crystals (rich in Ga_2O_3); B: enlarged view of the region marked by arrow in A; D: enlarged view of the Ga_2O_3-rich crystals shown in the circle in C; E: enlarged view of the Ga_2O_3-rich crystals at the tip of the arrow in C; F: glassy appearing flakes or film near to where the sample stuck to the cage wire.

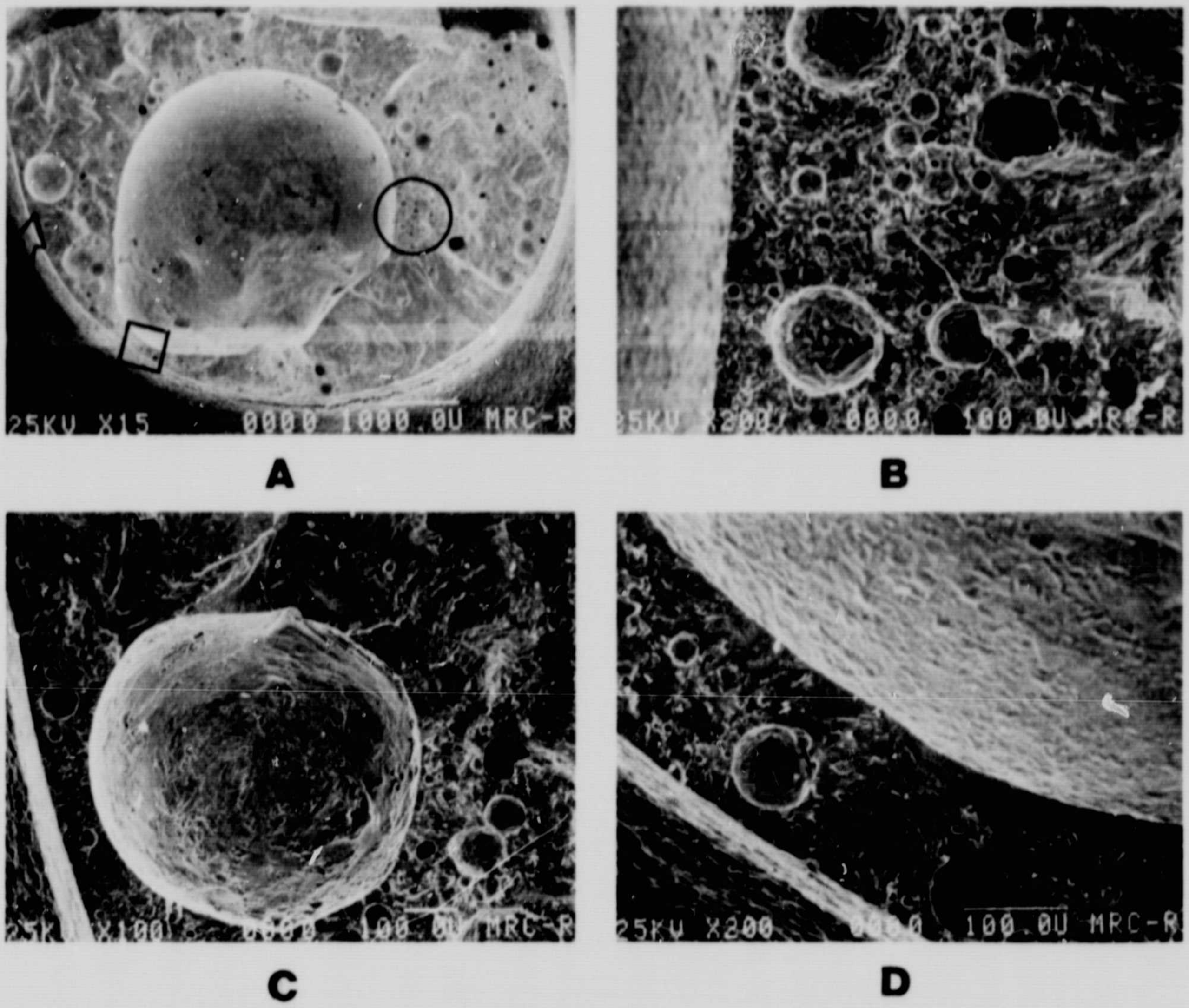


Figure 11. Appearance of the interior (fracture surface) of flight sample #3. A: large and numerous other smaller spherical bubbles, the top part of the sample was stuck to the cage wire; B: enlarged view of the circled region in A, showing the smooth wall (surface) of the large pore (left hand side) and the general appearance of the smaller pores; C: enlarged view of the bubble close to the external surface shown by arrow in A; D: magnified view of the region in the square in A, showing the wall between the large bubble and the external surface of the flight sample, minimum thickness of ~160 μm.

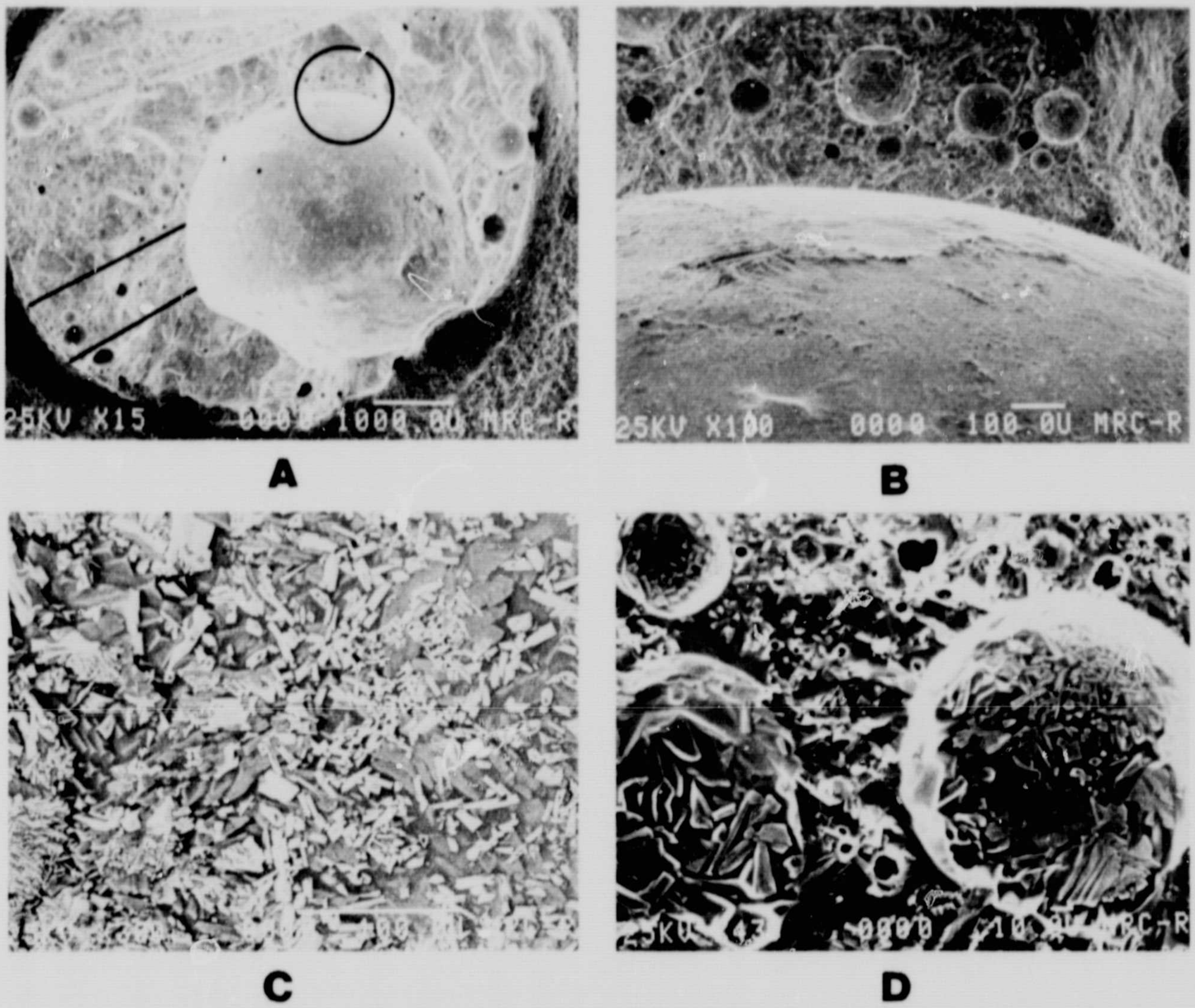
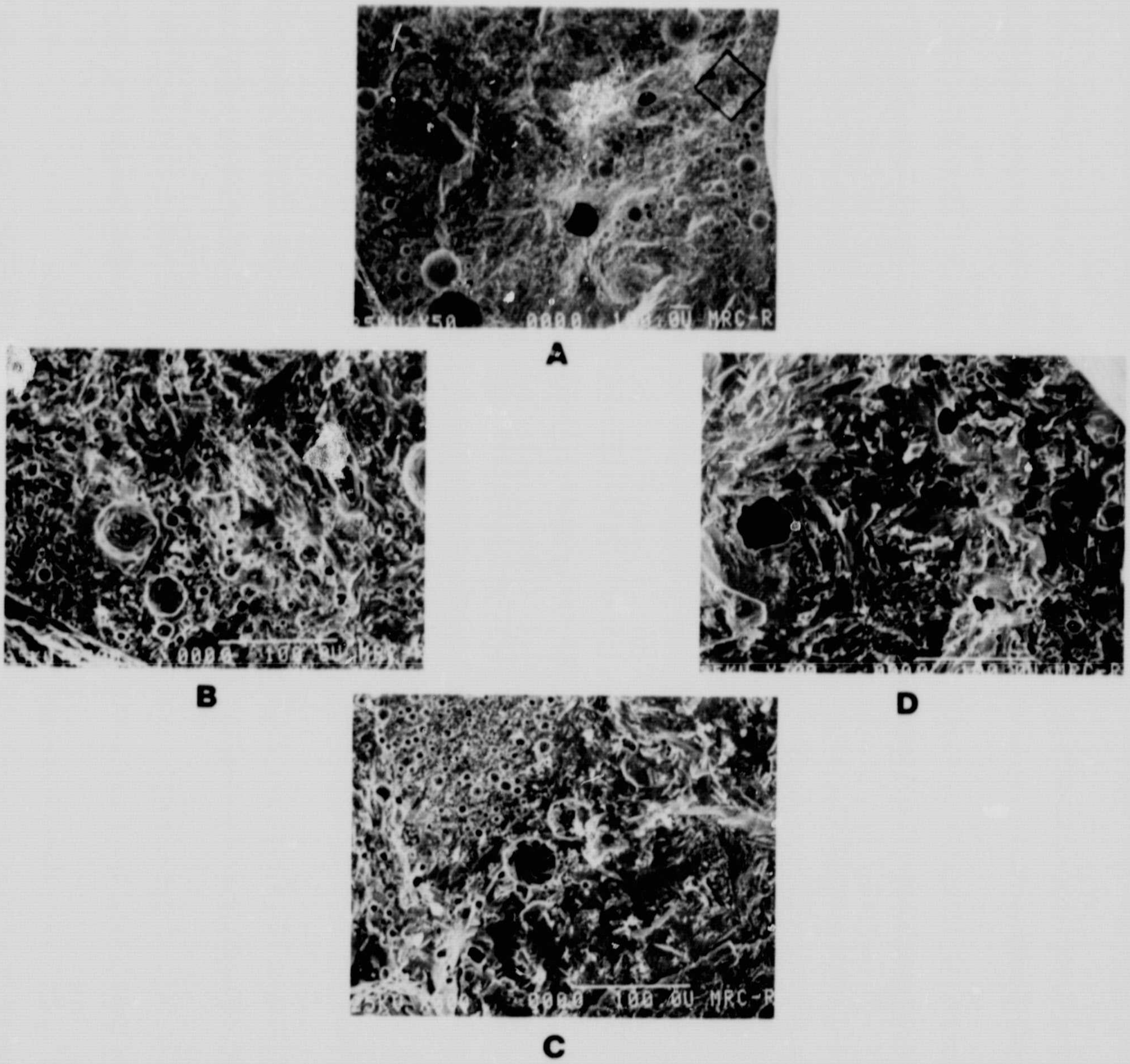


Figure 12. Interior (fracture surface) of flight sample #3, A: appearance of the large and other smaller spherical bubbles in the half of the sample opposite to that shown in Fig. 11A. The upper left hand corner shows the impression of saw cut; B: enlarged view of the circled region in A. The smooth region in the lower half of this figure is the wall of the large bubble; C: shape of the Ga_2O_3-rich crystals at the bottom of the large bubble; D: shape of the Ga_2O_3-rich crystals on the walls of other smaller bubbles, which are similar to those found for the large bubble (C).



A

B

D

C

Figure 13. Typical appearance of the interior (fracture surface) of flight sample #3. A: enlarged view of the region between the straight lines in Fig. 12A; B: enlarged view at the tip of the arrow in A; C and D are the magnified views of the regions in A in the circle and square, respectively.

which was uniformly distributed in the hot pressed precursor, has coalesced to form the large pore. This coalescence could be caused by spinning (rotation) of the sample, to currents within the melt, or by some other unidentified factor.

Another potentially important factor is the pores on the external surface (Fig. 9) of the flight sample. These pores (holes) probably resulted from the breaking of gas bubbles at the external surface. The significance of this evidence is that gas bubbles breaking at the external surface could produce forces that might contribute to sample instability and to its subsequent escape from the acoustic energy well. This is only speculation at this time since this is the first time that a hot pressed sample with significant internal porosity has been melted in the single axis acoustic levitator and there is no direct photographic evidence of bursting bubbles. However, this possible source of sample instability needs to be taken into consideration in assessing the operational performance of the levitator.

VI. CONCLUSIONS

1. The performance of the samples used in the flight experiment was satisfactory. No mechanical damage (due to the vibration of the space shuttle), chemical attack, or change in weight of the sample was observed. The procedures followed in preparing, handling, and storing the samples is satisfactory.

2. None of the glass forming samples were fully melted (as planned) due to the temperature of the acoustic levitator/furnace being too low. Sample 3 was the only sample showing any detectable change in physical appearance.

3. Sample 3 was partially melted and returned to earth stuck to the cage.
    a. This sample had obviously escaped the acoustic energy well for some still unknown reason.
    b. The appearance and partial melting of this sample is consistent with its being heated between 1300-1440°C for a few minutes as recorded in MEA/A-1.
    c. The large pore inside this sample may be due to the coalescence of a major fraction of the smaller pores initially present and homogeneously distributed in the precursor. This coalescence could be due to rotation (spinning) of the sample, currents within the melt, or by some other factor.
    d. There is evidence that some of the pores (gas bubbles) have burst at the external surface. It is speculated that a bubble breaking at the external surface could produce forces that might contribute to sample instability and its subsequent escape from the acoustic energy well.

4. The exact source of the different impurities on the external surface of the samples and the black flakes near the shroud gate is presently unknown. The source of the copper contamination and the discoloration of cage 3 is most likely due to the overheating and oxidation of the copper cooling shroud which did not fully retract from the furnace during the cooling of sample 3.

5. Because of equipment malfunctions, none of the scientific objectives for experiment 81F01 were attained on MEA/A-1. The basic questions regarding enhanced glass formation and precursor preparation procedures are still unanswered.

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