SQT

SD 76-SA-0029

SECOND INTERIM REPORT MANUFACTURING UNIQUE GLASSES IN SPACE

Contract NAS8-28991

Prepared for

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Space Division
Rockwell International

(NASA-CR-150067) MANUFACTURING UNIQUE GLASSES IN SPACE Interim Report, 1 Nov. 1974 - 31 Mar. 1976 (Rockwell International Corp.) 42 p HC A03/MF A01 CSCL 11D
N77-12083
Unclas
G3/12 56391

SD 76-SA-0029

SECOND INTERIM REPORT

MANUFACTURING UNIQUE GLASSES IN SPACE

Covering the Period from November 1, 1974, to March 31, 1976

Contract NAS8-28991

March 31, 1976

Prepared for

George C. Marshall Space Flight Center

Marshall Space Flight Center, Alabama 35812

Prepared by

Ralph A. Happe, Principal Investigator

Rockwell International
Space Division

FOREWORD

This report is submitted by Space Division of Rockwell International to the National Aeronautics and Space Administration's George C. Marshall Space Flight Center (MSFC) in accordance with Contract NAS8-28991. Prepared by Principal Investigator Ralph A. Happe, the report covers contract work on the Manufacturing of Unique Glasses in Space for the period from November 1, 1974, to March 31, 1976.

CONTENTS

ILLUSTRATIONS

TABLES

INTRODUCTION AND SUMMARY

The combination of circumstances attending the melting of materials in space presents the possibility of making glasses from substances which to date have been observed only in the crystalline condition. There is no need for a solid container during the melting and superheating portion of the manufacturing cycle. The only contact of the melt with its surroundings can therefore be a gaseous atmosphere or, if so desired, a vacuum. Thus it is possible to melt many high-melting-point materials that heretofore could not be successfully melted because of reaction with the crucible material. This advantage alone might permit the preparation of new substances as glasses if their viscosity becomes sufficiently high on cooling to suppress crystal growth.

In addition, space melting permits cooling without the use of a solid mold. Thus, many of the usual crystal nucleation sites are eliminated. Unless a given material can spontaneously nucleate on cooling, undercooling below the normal melting point will occur. If a sufficient amount of undercooling is accompanied by a sufficient increase in viscosity, crystallization will be avoided entirely and glass will result.

Studies of space glasses under the present contract have been confined to oxide glasses. It is felt that the applications for such glasses are more readily predictable than for the other materials. Also, many of the principles that will evolve from a study of oxide glasses, which can be melted in air, permit a more direct approach to non-oxide materials in the future.

REVIEW OF EARLIER CONTRACT WORK

The original objective of the present study, briefly stated, was to attempt to prepare terrestrially 6-mm (1/4-inch) boules of new glasses by using containerless melting techniques. To accomplish this objective, an air suspension melting technique was developed, and it is described, along with other work done in the earlier stages of the contract effort, in the First Interim Report (Reference 1).

A laminar flow vertical wind tunnel was constructed for suspending oxide melts that were melted using the energy from a CO_2 laser beam. The laser, with an output of approximately 5.4×10^{13} ergs/hour (1-1/2 kw), was available for this study at the Electronics Research Division of Rockwell International. Early experiments utilized commercial mullite as the starting material to develop techniques for working with the equipment.

The vertical wind tunnel is shown to the left in Figure 1 along with the optical bench and equipment used for focusing and directing the laser beam. It was found necessary to employ a silica probe, or sting, in contact with the melt. The sting, which is wet by the melt and typically supplies only a small portion of the supporting force, stabilizes the melt, presenting a relatively

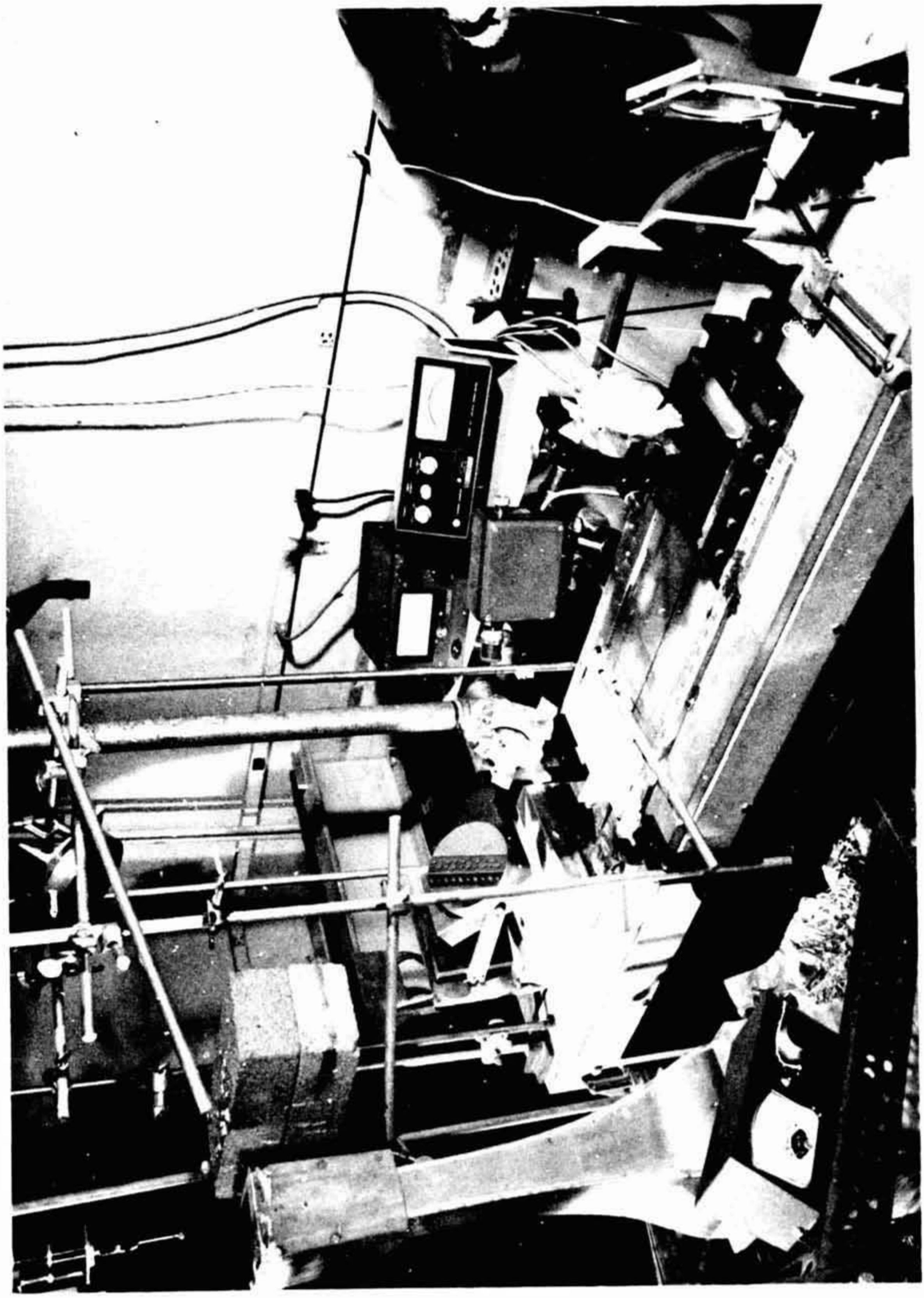


Figure 1. Optical Bench for Focusing and Directing Laser Beam

fixed target for the laser beam. A photograph of the sting with a melt attached is shown in Figure 2. (To obtain the photograph, the laser beam was directed behind the solidified melt and was made visible by sprinkling talcum powder in its path.)

After a technique was developed, seven oxide compositions selected from previous work were studied. Two of these (i.e., 80 w/o gallia + 20 w/o calcia and 40 w/o lanthana + 40 w/o alumina + 20 w/o calcia) proved to be good glass formers in the 6-mm size using the techniques developed. Additionally, glasses were prepared in the 6-mm size from several glass compositions not included in the earlier studies. All of these latter glasses contained CaO as an addition agent. Finally, a concept for an in-space glass melting experiment was developed for use in conduting sounding rocket experiments under near zero-gravity conditions.

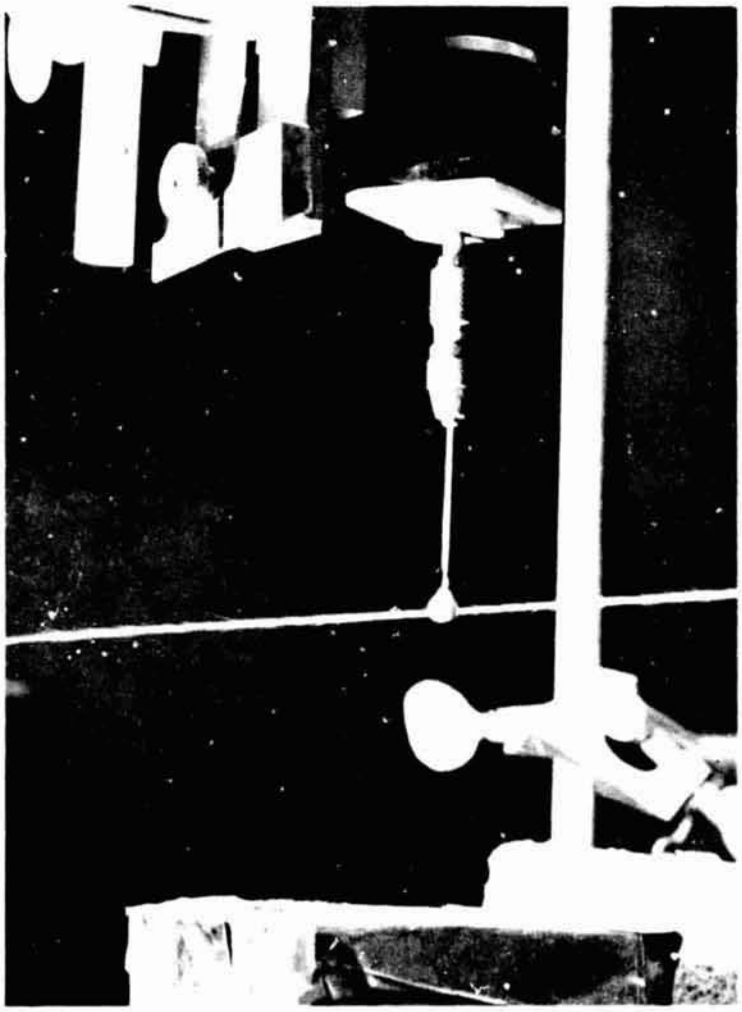


Figure 2. Setup for Melting Oxides

SUMMARY OF WORK DONE DURING THE CURRENT REPORTING PERIOD

During the current reporting period, 6-mm boules of the two compositions (i.e., gallia-calcia and lanthana-alumina-calcia) were submitted to the Perkin-Elmer Corporation for a study of stress relieving, sample fabrication, and optical properties. The presence of striae prevented the determination of optical properties for the ternary composition and reduced the hoped-for accuracy in the determinations for the binary composition. Nevertheless, the binary gallia-calcia glass shows promise for optical applications in the visible spectrum.

In cooperation with Owens-Illinois, Inc., a study was performed of the containerless melting of several improved lasing glass candidate compositions. Preliminary results indicate that space processing shows much promise for improved laser glasses which cannot be made terrestrially because of devitrification.

A major thrust of the present portion of the program has been the development of cinematography techniques for studying the melting and cooling phenomena occurring during the laser melting/air suspension process. Considerable progress has been made along these lines, and we are confident that, with minimal further development, temperatures at critical points in the cycle can be read from the motion picture film with reasonable accuracy.

Finally, a significant portion of the program effort has continued to be devoted to supporting a series of sounding rocket glass experiments. The portion of that effort accomplished with the support of this program is described.

EXPERIMENTAL WORK AND RESULTS

SAMPLE PREPARATION AND OPTICAL PROPERTY MEASUREMENTS

The work performed for Rockwell International by the Perkin-Elmer Corporation of Norwalk, Connecticut, is summarized in this subsection. A detailed report is contained in Reference 2.

Samples of the gallia - 20 w/o calcia and the 40 w/o lanthana - 40 w/o alumina - 20 w/o calcia glasses shown in Figures 19 and 12 of Reference 1 were submitted to Perkin-Elmer for determination of stress relief annealing temperatures, fabrication into specimens suitable for measurement of optical properties, and measurement of index of refracion at three wavelengths of light and transmission at various wavelengths in the visible portion of the spectrum. The initial submittal to Perkin-Elmer was from samples prepared in 1974 as described in Reference 1. The gallia-calcia glass was of a pale bluish-grey color and the lanthana-alumina-calcia glass was of a light straw color.

In early 1975, a second shipment of hot-pressed rods of each composition was received from the supplier, the Haselden Company of San Jose, California. More glass boules were prepared using a 4-mm diameter silica probe. The second lot of gallia-calcia yielded glass of a pale straw color as contrasted with the bluish-grey color of the earlier batch. The newer batch of the lanthana-alumina-calcia glass was free of the spalling and gassing problems encountered with the earlier batch. The color of the glass produced from the newer batch of starting rods of the ternary glass was similar (a pale straw color) to that of the glass prepared from the earlier batch. Samples of glass boules of both compositions prepared from the newer material were sent to Perkin-Elmer.

Devitrification Temperature and Stress Relief Annealing

The samples received by Perkin-Elmer were found under crossed Polaroid examination to contain a high level of residual stress. This was expected in view of the higher expansion coefficient which may be presumed for the experimental glasses as contrasted with the very low expansion coefficient of the fused silica probe.

Accordingly, each composition was heated in an annealing furnace to a series of temperatures in 50°C increments. The ternary glass devitrified at 910°C and the gallia-calcia glass devitrified at 830°C. In subsequent runs, it was found that annealing at 860°C and 760°C, respectively, for the ternary and binary glass was effective in producing relatively stress-free samples. However, it was noted that in those samples with the fused silica probes still attached, stresses in the immediate vicinity of the probe were not completely removed. The annealing runs were made on the 1975 samples.

Sample Fabrication

Rectangular plates[1] were prepared from stress-relieved samples of the glass boules. It was noted that the hardness of both glasses was close to that of sapphire, 9 on the Moh scale. This may be compared with typical hardnesses of 4.5 to 6.5 for silicate glasses.

Eight samples were prepared and are shown magnified 10 to 15 times in Figures 3 and 4. All samples were reported relatively free of birefringence after fabrication. All samples contained striae, which are areas of unequal index of refraction. The samples were photographed with backlighting to emphasize the striae, which can be seen as patterns in the specimens. If there were no striae or other defects present, the samples photographed under these conditions would be featureless. Two of the samples of the lanthana-alumina-calcia glass (Figures 3a and 3c), also show cracks which formed, presumably, during the polishing operation. In neither case is the fracturing complete, the samples still being in one piece. The subject of striae is discussed further in a later section.

Optical Properties Measurements

Because of the excessive striae in the lanthana-alumina-calcia glass, it was impossible to obtain index of refraction measurements. Index values for three wavelengths of light were obtained for one of the 1975 gallia-calcia samples (Figure 3c). Because of striae, the accuracy of measurement was no better than ± 5 in the fourth decimal place. Values determined are:

Wavelength, Å	Spectral Line	Index of Refraction (n)	Temperature, °C	Pressure, mm. of Hg
4800	Blue Cd (F')	1.7853	25	762.4
5461	Green Hg (e)	1.7805	26.8	759.3
6438	Red Cd (C')	1.7698	24.9	762.4

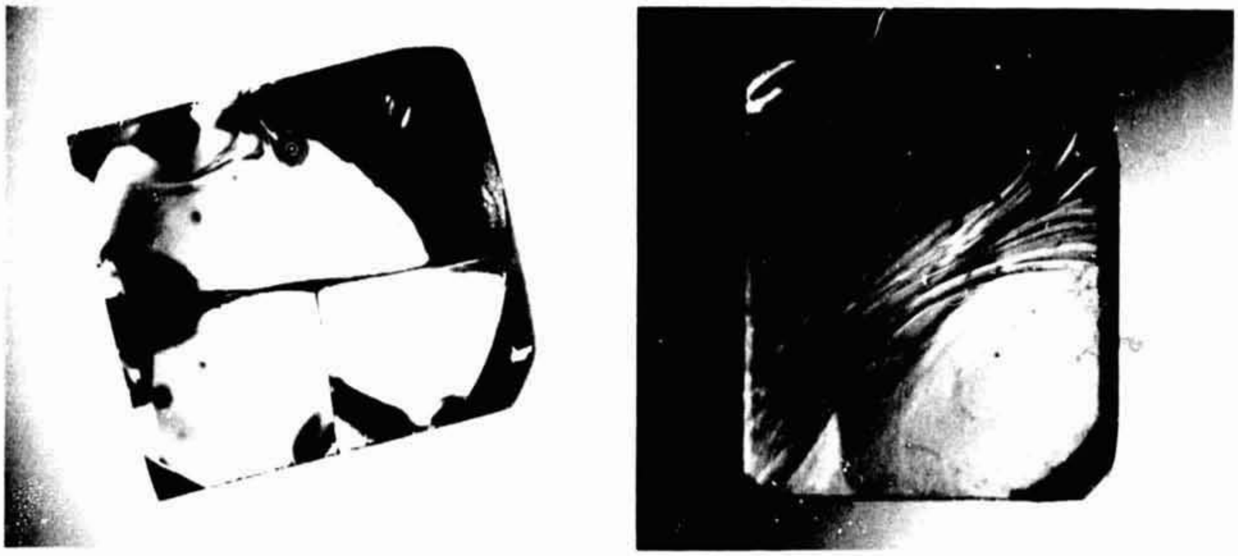
An attempt was made to measure refractive index of one of the 1974 gallia-calcia samples (Figure 4d). Because of excessive striae, which causes broadening and dimming of the refracted rays, the index values obtained were considered accurate only to the third decimal place. Values are:

Wavelength, Å	Index of Refraction (n)	Temperature, °C	Pressure, mm. of Hg
4800	1.792	23.9	753.4
5461	1.779	23.0	752.8
6438	1.769	23.6	762.6

Within the limits of accuracy obtained, there appears to be agreement between the index values of the two samples at the two longer wavelengths.

---

[1] Earlier plans called for the preparation of 60° prisms. The preparation of rectangular plates (90° prisms) permitted both the index of refraction (using a Grauer refractometer) and transmission measurements to be performed on the same specimen.



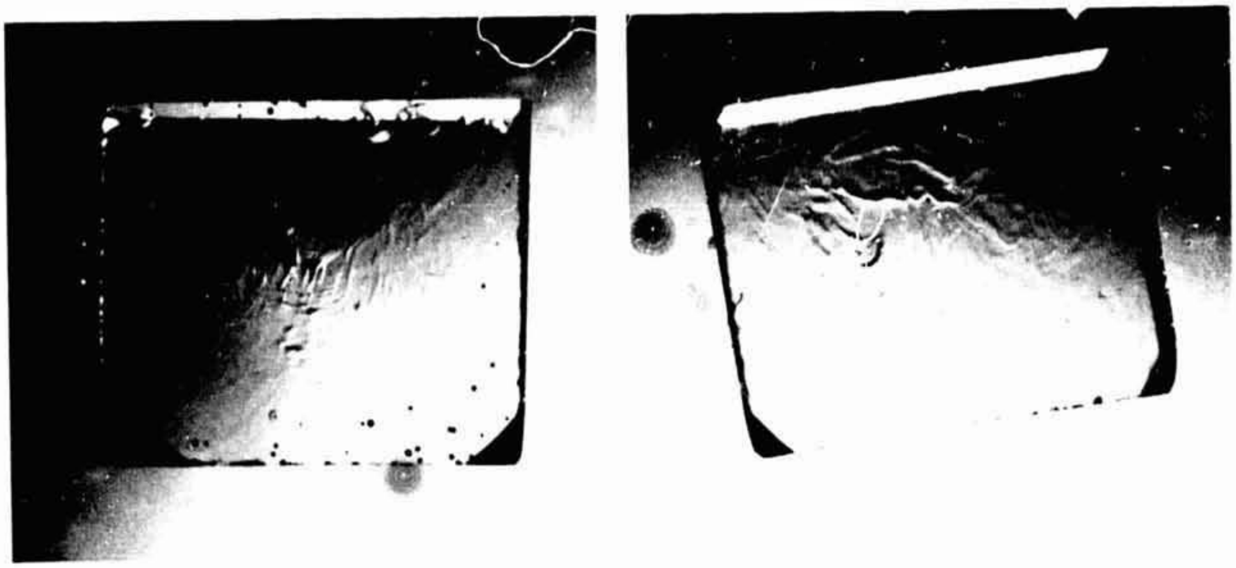
a. Prepared 3/20/75-Striae and Cracks

b. Prepared 3/20/75-Striae

c. Prepared 3/20/75-Striae and Cracks

d. Prepared 10/26/74-Striae

Figure 3. Lanthana-Alumina-Calcia Glass Specimens Prepared for Optical Property Determination
(All samples were photographed with front and back lighting)



a. Prepared 3/20/75—Straie (Index values measured to ± 0.0005)

b. Prepared 3/20/75-Straie

c. Prepared 3/20/75—Straie

d. Prepared 6/17/74—Straie (Index values measured to ± 0.005)

Figure 4. Gallia-Calcia Glass Specimens Prepared for Optical Property Determination
(All samples were photographed with front and back lighting)

The index values at 4800 A, however, are definitely not in agreement, even within the rather poor limits of accuracy obtained. It is possible that the lack of agreement in the blue is real and may be associated with the different color of the two samples. The 1975 glass, which gave a lower index value in the blue, was of a straw color, while the 1974 glass was of a blue-grey color.

The values for the 1975 glass were plotted on a large graph and index values for the hydrogen F, helium d and hydrogen C lines were read from the curve. These values are as follows:

Line	Wavelength, Å	Index of Refraction
Hydrogen F	4861	1.7847
Helium d	5876	1.7766
Hydrogen C	6563	1.7680

Using these values it is possible to calculate the Abbe number, ν_d:

$$\nu_d = \frac{n_d - 1}{n_F - n_C} = 46.5$$

The 1975 gallia-calcia glass is shown plotted on the n_d - ν_d map in Figure 5. It falls just within the area covered by the Schott commercial optical glasses. Commercial optical glasses with similar n_d - ν_d combinations are:

Manufacturer	Designation	n_d	ν_d
	1975 Gallia-Calcia (777465)	1.7766	46.5
Schott	LaF 21 (788474)	1.788309	47.39
Schott	LaF 24 (757478)	1.757192	47.81
Schott	LaK 17 (788505)	1.788470	50.48
Schott	LaF 10 (784439)	1.784431	43.88
Eastman Kodak	EK 110 (697562)	1.69680	56.15
Eastman Kodak	EK 450 (804418)	1.80370	41.80
Corning	LaF-74 (744-448)	1.74400	44.77

These commercial glasses are of complex composition and depend on rare earth oxide additions to obtain their combination of properties. It would appear, then, that the simple (binary) gallia glass has considerable promise as a base composition to fill in an important area of the n-ν map without requiring the use of thoria or rare earth oxides.

A plot of refractive index versus wavelength is given in Figure 6 (solid line). It is noteworthy that the curve is concave-down in contrast to the characteristic concave-up shape of virtually all silicate, borate, and phosphate glasses. A plot for LaF 21, the Schott glass with n_D - ν_D closest to the gallia-caleia glass, is shown as a dashed line in Figure 6 for comparison. Inspection shows that no combination of measurement errors within the ± 0.0005 reported by Perkin-Elmer would alter the concave-down nature of the gallia curve.

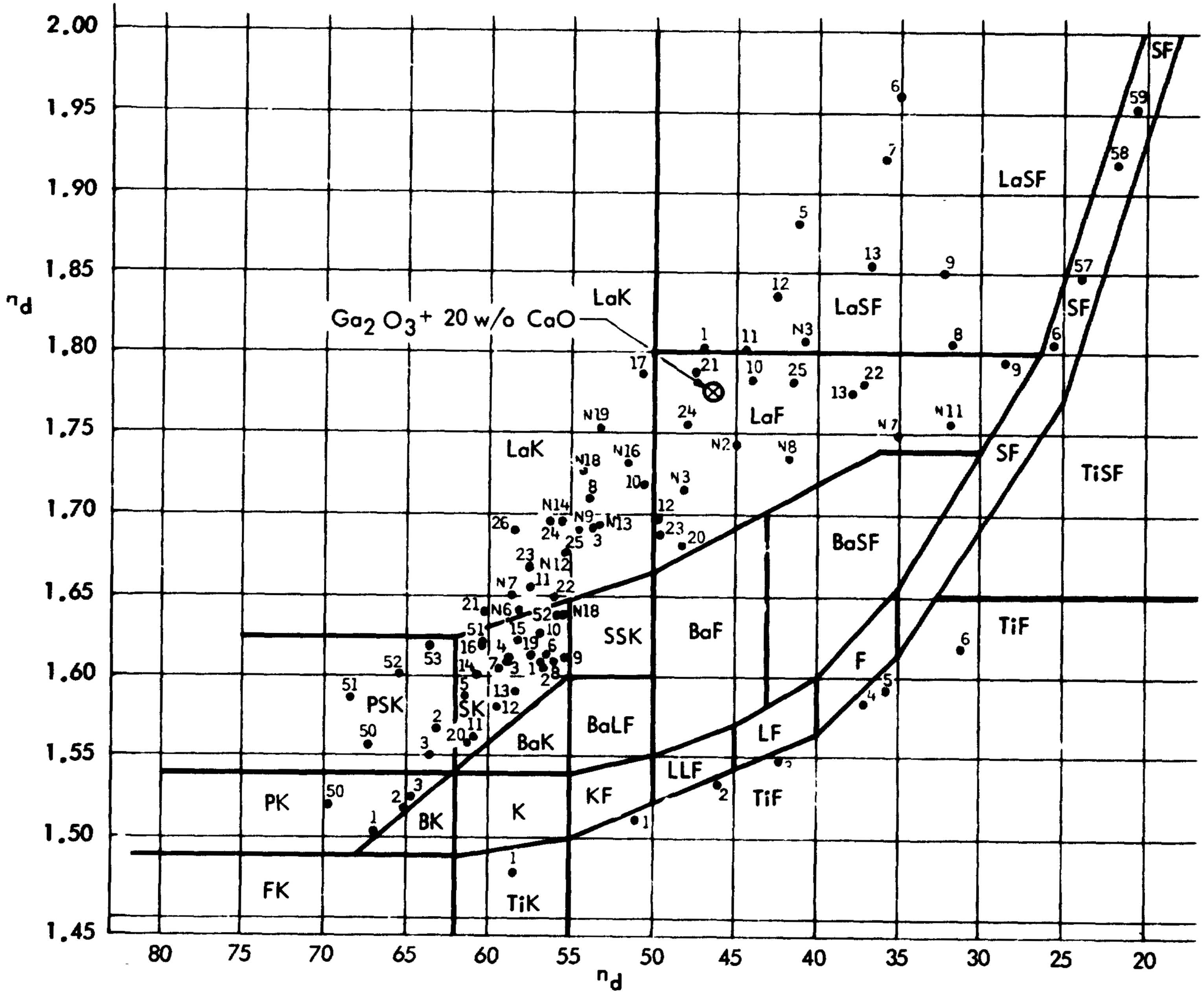


Figure 5. Diagram of Optical Glasses

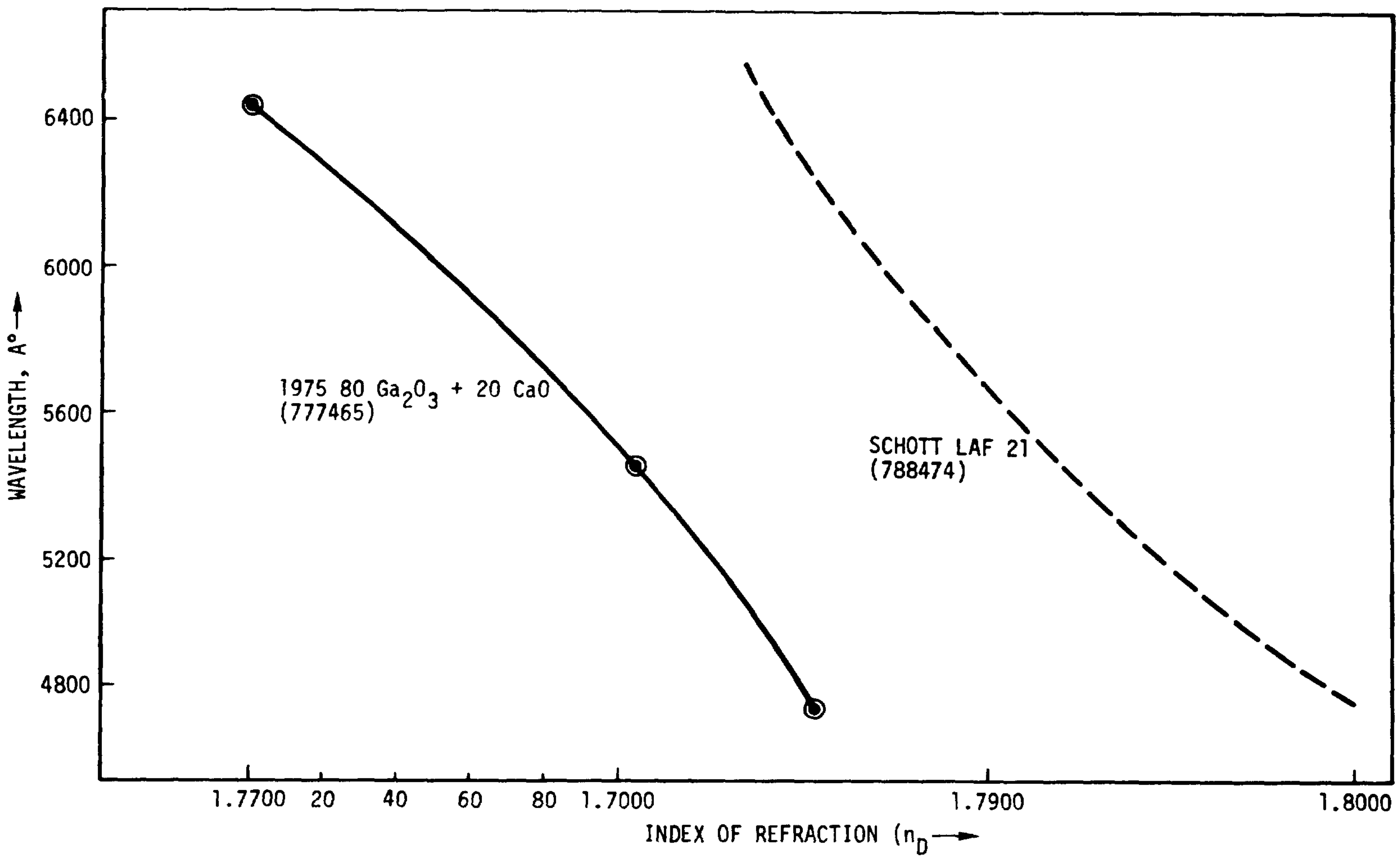


Figure 6. Wavelength Versus Index of Refraction for Ga_2O_3 - CaO Glass and Schott LaF 21 Glass

Therefore it can be assumed that this shape is real for this particular sample, at least.

The 1975 gallia-calcia glass appears to be exhibiting "anomalous" dispersion as discussed in Jenkins and White (Reference 3). This means that there may be an absorption band in the near infrared, closer to the visible portion of the spectrum than is the case with "normal" glasses. Such an absorption band can be explained in two ways: either the placement is intrinsic to the gallia-calcia glass or the band is caused by impurities. If the first explanation turns out to be true, it is possible that the ultraviolet absorption band, which begins in the 4000 to 2000 Å region for all known glasses, is also displaced to lower wavelengths for the gallia glass. If this should prove to be true, the gallia-calcia glasses may have potential application as an ultraviolet transmitter. Unfortunately, the sample of 1975 gallia-calcia glass shown in Figure 3c has been irretrevably lost. As of this writing limited funds do not permit the stress relieving and preparation of another sample to measure transmission in the ultraviolet and near infrared.

Transmission measurements were obtained by Perkin-Elmer for the ternary glass and for the 1974 gallia-calcia glass (which exhibited normal dispersion). Transmission over the range 3300 Å (0.33 μ) to 8000 Å (0.8 μ) is similar to ordinary optical glass. Neither showed an absorption band in the red end of the spectrum measured. Both glasses showed cutoff (50-percent transmission) at 4000 Å.

A Bausch and Lomb paper (Reference 4) discusses the role of partial dispersions in secondary spectra correction. Using formulas given in the paper, partial dispersions were calculated for the 1975 gallia-calcia glass as follows:

$$P_{FD} = \frac{n_F - n_D}{n_F - n_C} = \frac{1.7847 - 1.7764}{1.7847 - 1.7680} = \frac{.0083}{.0167} = 0.50$$

$$P_{DC} \quad \frac{n_D - n_C}{n_F - n_C} = \frac{1.7764 - 1.7680}{1.7847 - 1.7680} = \frac{.0084}{.0167} = 0.50$$

Assuming the accuracy of the original measurements (i.e., ±0.0005) is maintained in the reading of n_F, n_D, and n_C from the graph, the true values of both P_{FD} and P_{DC} can be expected to fall into the 0.45 to 0.55 range. Such poor accuracy may be considered unacceptable for "normal" glasses, where differences of 0.002 are considered significant. However, because of the large difference in these values from "normal" glasses (whose P_{FD} falls within the range 0.690 to 0.710 and whose P_{DC} falls within the range 0.280 to 0.300), it may be safely concluded that the partial dispersion ratios of the gallia glass are indeed unusual. Perhaps gallium oxide may prove to be a powerful addition agent for conventional glasses to develop new families of glasses for secondary spectrum correction.

Discussion of Striae

The presence of striae in all of the gallia-calcia and lanthana-alumina-calcia glass samples studied by Perkin-Elmer must be considered a major problem.

Because of striae, it was possible to measure index of refraction of only one of four of the gallia-calcia glass samples prepared to an accuracy approaching that required for a reasonable assessment of the optical properties. None of the lanthana-alumina-calcia glass specimens prepared could be measured at all.

Since striae are a manifestation of lack of homogeneity in the glass, it seems pertinent to attempt to arrive at an understanding of the cause for such inhomogeneity. There appear to be two possible explanations:

1. Insufficient mixing of the basic ingredients of the melt (e.g., gallium oxide and calcium oxide in the case of the gallia-calcia glass).
2. Silica from the probe being continuously dissolved during the melting process and causing areas of high silica content (and, therefore, lower index of refraction) in the finished boule.

Insufficient Mixing

All samples submitted to Perkin-Elmer were prepared from hot-pressed rods supplied by the Haselden Company of San Jose, California. The hot-pressed rods were prepared from the pure constituent oxide powders. The powders were thoroughly mixed and blended before hot pressing. It is quite possible that the individual constituent oxide particles did not interdiffuse enough during hot pressing to result in a homogeneous material. Therefore, it would appear reasonable that any lack of homogeniety in the hot-pressed rods would be of a micro- rather than a macro- nature. It may also be pertinent to note that there was no gross evidence from the handling and melting behavior of the rods that a detectable amount of macro- segregation was present.

The motion picture studies (to be discussed later) demonstrate that there is a large amount of swirling turbulence in the melt with the air suspension/laser technique. It would therefore appear that the possibility that striae are caused by improper mixing is extremely remote. This conclusion is further amplified by the consideration that the viscosity in the molten state for both compositions is very low, probably approaching that of water.

Silica Contamination

Having all but eliminated improper mixing of the basic ingredients as a cause of striae, we must point the finger of suspicion strongly to the silica probe as the prime cause of striae. Chemical analysis has shown in the past that silica pick-up can be held to less than 1 percent for these glasses. Chemical analysis, however, reveals nothing about how the silica which is picked up is distributed. Therefore, a good case can be made for the silica probe being the cause of striae.

During the melting process the silica, being soluble in the molten glass sample, is continuously being dissolved. Since fused silica has a high viscosity it is not difficult to imagine that it never has an opportunity to become uniformly distributed. The continuous feeding of the melt with silica, plus the stirring action within the melt, could easily result in the striae patterns observed in Figures 3 and 4.

In the forthcoming sounding rocket experiment program the silica probe may still be used. However, the lack of turbulence expected when melting under near-zero-gravity conditions should result in an entirely different type of pattern. The continuous dissolving of silica from the probe during melting may result in a uniform composition gradient across the sample. If this happens, there should be a corresponding continuous variation in refractive index from the probe-sample interface to the opposite surface, perhaps analagous to solid-solid diffusion. The ultimate solution to the homogeneity problem may have to await the development of space melting procedures that avoid all contact with the melt, except for the melting atmosphere.

PRELIMINARY EXPERIMENTS WITH LASING GLASS

Owens-Illinois, Inc., under contract to the Jet Propulsion Laboratory performed a study (Reference 5) which demonstrated that improved lasing glasses theoretically could be prepared in space by increasing the calcium oxide content of the commercial glasses currently marketed by Owens-Illinois. It was shown, for example, that increasing the CaO content from 20 to 30 percent would increase the lasing efficiency by about 10 percent. Since an increase in the CaO content also increases the devitrification tendencies of the glasses, it is not feasible to prepare high-quality improved glasses terrestrially. The summary from the Owens-Illinois final report is presented verbatim:

"The purpose of this six-month study was to consider the feasibility of producing improved laser glass material in an outer space laboratory. The unique advantage of outer space, particularly germane to this study, is the zero-g condition or weightlessness. This condition may be exploited to melt and form glass in outer space without relying upon a container. Since the container walls and impurities introduced into the bulk of the glass from the container walls serve as heterogeneous crystal nucleation sites, the elimination of the container will greatly reduce the ability for crystal nuclei to form in the melt and thus deter the devitrification process.

"A major portion of this study was devoted to classical homogeneous nucleation calculations and crystal growth calculations for a laser glass system, which are appropriate for the conditions of an outer space laboratory. We demonstrate that in the absence of heterogeneous nucleating sites our experimental laser glass material may be readily formed crystal free.

"In addition, a number of experiments were performed in order to obtain information essential for the above calculations and to provide further evidence for the feasibility of producing our experimental laser glass in outer space and demonstrate the impossibility of its crystal-free production on earth. In particular, thermal gradient oven experiments, DTA (differential thermal analyses) studies, liquidus determination, and x-diffraction analyses were performed to elucidate the fundamental phase behavior of the laser glass system under investigation. Furthermore, SAXS (small-angle x-ray scattering) data were collected to study the possible existence of a phase separation mechanism acting as a precursor to the nucleation of the crystal phases observed. No evidence of a liquid-liquid immiscibility was found for the glass prepared via the standard air-quench procedure. Also, a splat-cooling experiment was carried out to observe the crystallization behavior exhibited by the laser glass under very rapid cooling rates. It was observed that although small surface crystallites did form, the interior of the sample was crystal free. This result serves to illustrate the point that earth fabrication of this material will always be marred by crystallization due to surface contact, regardless of the cooling rate. Yet, it also indicates that in principle one may produce, in bulk, this material crystal free. Of course, on earth it is not feasible to produce laser glass by a splat-cooling technique (even if surface crystals did not appear) since only thin samples may be prepared in this manner.

"Finally, the economics associated with laser glass production was assessed. We illustrated how a small increase in laser efficiency could produce a sizeable cost reduction in the USA laser fusion program. Furthermore, the fabrication of more efficient glass lasers could open up new markets for this product hitherto untapped."

In view of the very favorable results achieved with the Owens-Illinois study, it was agreed that the interests of the NASA space processing program would be well-served by entering into an informal agreement in which samples prepared by Owens-Illinois would be melted by Rockwell using the air suspension/laser melting technique developed under the current MSFC-sponsored program. The JPL and MSFC COR's both concurred with this arrangement.

The section which follows describes the preliminary work from Rockwell's point of view. The work began in July, 1975, upon receipt of the first lot of starting material from Owens-Illinois, shortly after their new contract with JPL was in effect. Most of the work performed during this reporting period was of a preliminary nature aimed primarily at evaluating for Owens-Illinois the suitability of various starting material preparation techniques. Some of the batch-crystalline material of the 35 and 40 percent calcia compositions also were included in some of the cinematography studies and the findings are reported in a later section of this report. Table 1 summarizes the preliminary tests performed by Rockwell. The samples are listed in the order in which they were received. It is the writer's understanding that the nominal composition of all samples received from Owens-Illinois is as follows, in mol percent:

Li_2O — 27.5

Al_2O_3 — 2.5

Nd_2O_3 — 0.5

CeO_2 — 0.16

$SiO_2 + CaO$ — 69.3

Based on the results obtained and reported in Table 1, the following conclusions represent the writer's opinion of the material supplied to date:

1. The best material is the 35-percent CaO crystalline material (sample No. 1). It is a good glass-former with the preparation techniques used. The starting material is rugged and quite free of gas.

2. The second choice is the 40-percent CaO crystalline material. It is less rugged than the 35-percent CaO material and is more gassy. It appears to be a marginal glass-former with the techniques used.

3. The 30-percent CaO material is an excellent glass-former but all samples supplied had serious handling, spalling, and gassing problems.

4. The cold-pressed 35-percent CaO material confirms the results obtained with the crystalline material of the same composition cooled from the batch so far as glass formation is concerned. However, the material is too fragile to be handled effectively.

The first three conclusions suggest the possibility that a good starting material might be obtained for the 30-percent CaO composition by cooling from the batch in platinum and introducing some crystalline (devitrified glass) material into the melt while it is cooling.

Some of the samples prepared were mailed to O-I. Their preliminary tests indicated that the 40-percent CaO glass boules suffered severe lithia loss (about 7 percent) and silica pickup (from the probe). Silica pickup was about 6 percent. The 35-percent CaO glasses showed a smaller lithia loss (about 3 percent) along with a similar silica pickup (6 percent).

Liquidus temperatures have been determined for some of the lasing glass candidates by both Owens-Illinois and the Rockwell Science Center. Owens-Illinois used differential thermal analysis (DTA) and the Science Center read the liquidus both on heating and cooling using an optical pyrometer on the surface of the melt which was induction-melted using a platinum crucible. Initial results were as follows:

Percent CaO (mol. %)	Liquidus °C	Determined by	Method
30	1010	O-I	DTA
35	972	O-I	DTA
40	1016	O-I	DTA
40	1140	Science Center	Optical Pyrometer

Subsequent investigations by O-I using direct observation of the melt surface during cooling showed that a small amount of primary phase nucleated on the surface of the 40-percent CaO composition at a temperature well in excess of the temperature determined by DTA. Since the amount of phase formed was very small, it apparently escaped detection in the DTA. Until further work can be done, it must be tentatively concluded that the true liquidus temperatures for all three compositions fall into the range 1070 to 1140°C.

During the cinematographic study to be described later, it was discovered that our melting procedure produces superheat temperatures typically in the range 1750 to 2200°C regardless of the composition being melted. Since these

Table 1. Lasing Glass Samples Evaluated for Owens-Illinois, Inc.

I.	35% CaO crystallized material (cooled from the batch)	Laser melted with no spitting or spalling. Appeared relatively gas-free. Difficult to transfer to probe because of low viscosity when molten. Readily formed 100% glass when laser-melted on probe with air suspension.
II.	30% CaO glass material (identified by O-I as 74064 A2)	Spalled severely when touched by laser beam. Managed to melt a portion of the boule supplied with the laser beam to form a puddle. Part of the remelted material was crystalline - presumably having devitrified at a temperature below the crystalline solidus during the laser heating operation. Unable to transfer to the probe for air suspension tests because of the severe spalling problem. Test was inconclusive.
III.	30% CaO cold-pressed material	One of three discs was intact when package was opened. About one-half of each of the other two samples had reverted to powder. The indicating dessicant included in the package (blue dririte) had partly changed color indicating the presence of moisture. The intact sample spit a bit (gassing) when laser melted and transferred to a probe. Sample was about 95% glassy as transferred to the probe. Tests had to be discontinued because of extreme difficulty in handling fragile material. Had it been possible to continue tests, no doubt would have obtained 100% glass with ease using air suspension melting. This was first sample tested on this program that was largely glassy as transferred to probe.
IV.	35% CaO cold-pressed material	All three discs received still intact. Dessicant had partly changed color. First sample melted on a probe dropped from the probe when melted and was caught by the stainless steel screen at the top of the wind tunnel exit. This sample was 100% glassy as examined under low power with a hand glass. This confirms earlier observations that this composition is a good glass former. This was the first time in history of program that sample cooled on screen was other than 100% crystalline. Tests had to be discontinued because of extreme fragility of pressings received.
V.	40% CaO cold-pressed material	Two of three discs received intact. Third was split into two pieces. Dessicant had begun to turn color. Sample was very gassy when melted with laser beam. Numerous melting attempts were made with probe and air suspension. Material had great tendency to climb (and bury) probe. Obtained several cracked samples that were almost entirely glassy. Invariably had to remelt several times to avoid devitrification on cooling. Composition appeared to be be borderline glass-former.
VI.	40% CaO crystallized material (cooled from the batch)	Laser-melted fairly well but there was some indication of gassing. Not as strong as 35% CaO crystalline sample (I). Spalled moderately when struck by laser beam. Numerous probe/air suspension melting tests performed. Never obtained glass on first air suspension melting attempt - usually obtained (cracked) glass on second attempt (remelt). There was evidence that one or more (Li_2O?) constituents boiled off during melting.
VII.	40% CaO pellet prepared by MOD (metal organic derivative) technique. (material claimed by O-I to be amorphous) - Pellet A	Melts and handles nicely. Very gassy. Transferred to probe easily and produced glass on first attempt with probe/air suspension technique. Sample as received appears to have very low apparent density.
VIII.	Similar to VII - Pellet B	Behaved similarly to Sample VII. Very gassy. No probe melting tests performed.
IX.	Similar to VII - Pellet C	Behaved similarly to Samples VII and VIII. Very gassy. No probe melting tests performed.

temperatures are obviously too high for a material with a liquidus temperature below 1140°C, it was decided to prepare some more specimens with the laser power attenuated. The method chosen to accomplish this was to detune (misalign) the laser to cut the beam power to about a third of that used for preparing the earlier melts.

New melts were prepared from both the 35- and 40-percent CaO lasing glass candidate materials (samples I and VI of Table 1). These melts were prepared late in the reporting period and no motion pictures have been obtained to date. However, it was possible to prepare glass samples from both compositions with much lower superheat temperatures. The temperatures reached were sufficiently lower than that of the earlier melts that the samples could not be observed effectively through the cobalt blue glass blower's goggles normally used. The newer melts were therefore prepared without protective glasses, an indication that the temperatures were much lower. Less difficulty was encountered with probe climbing so that uncracked boules were obtained in many instances. Some of the boules prepared in this manner are shown in Figure 7. Several samples were mailed to O-I for chemical analysis. Results have not been obtained as of this writing.

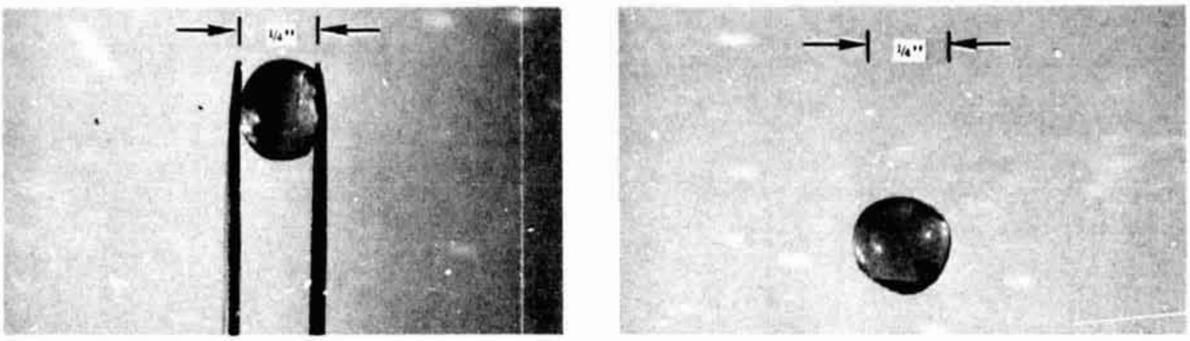
CINEMATOGRAPHY STUDIES

Technique Development

One of the principal objectives of the work performed during the current reporting period has been the development of motion picture techniques for studying the melting and cooling of oxides with the laser melting/air suspension technique. Motion pictures of the freezing of mullite prepared during the earlier portion of the program revealed much about the nature of nucleation and crystal growth during containerless cooling. It was decided to place major emphasis on motion pictures as a way of understanding what is happening during the processing of the experimental boules.

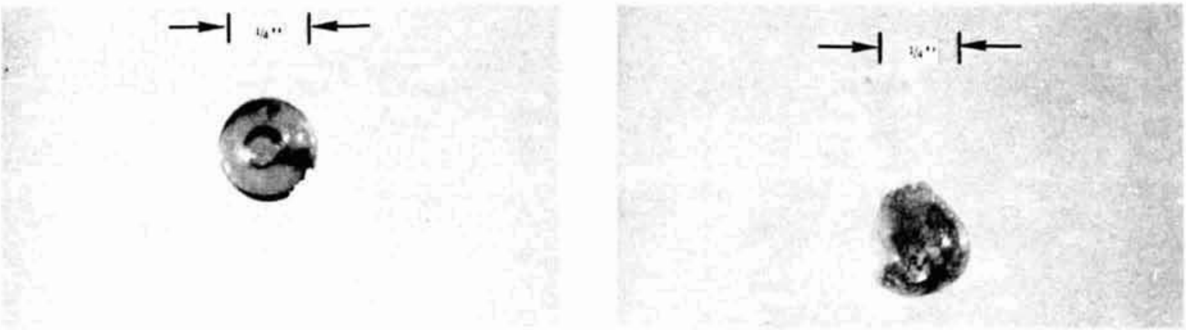
During the preparation process developed for this study, a typical 6-mm diameter boule is heated to temperature as high as 2200°C from room temperature in less than 12 seconds. Cooling to temperatures below about 600°C occurs typically in less than 15 seconds. Many critical events therefore happen so rapidly that it is difficult or impossible to follow them adequately with real-time observation. In addition, it is very difficult to obtain direct measurement of temperatures or to know when to read them. Therefore the use of slow-motion cinematography appears to be an ideal method for studying the process. In theory, it is possible to record the entire process on motion picture film. The developed film can be played back at any speed desired. Critical events can be identified as occurring in designated frames, and densitometer readings obtained on portions of the frames of interest. If the film/development procedure has been properly calibrated, the densitometer readings can be converted to temperatures.

While this procedure sounds easy and relatively straightforward, there are a number of difficulties that must be overcome before reasonable data can be obtained. Some of these difficulties are as follows:



a. 35% CaO Laser Glass--Prepared with laser beam attenuated to 42% normal and remelted once

b. 40% CaO Laser Glass--Prepared with laser beam attenuated to 33% normal--remelted twice; note devitrification (two darker zones)



c. Same sample as Figure a--Fracture face down

d. 40% CaO Laser Glass--Laser beam attenuated to 33% normal--remelted once--approximately 50/50 glass and crystal (note tapering of probe indicating dissolution of silica)

Figure 7. Lasing Glass Samples Prepared With Attenuated Laser Power

1. With the process under study, alignment of the camera with the subject must be precise. Slight misalignment of the camera or subject can result in the subject not appearing in the frame at all.

2. Since the radiant energy from the subject is a function of temperature to the fourth power, a temperature range of only several hundred degrees can be recorded appropriately with a given film exposure. The range of interest in the containerless melting process is on the order of 1000°C or greater. Therefore one cannot obtain accurate superheat temperatures and accurate crystallization temperatures, for example, from the same scene, even when shooting with wide latitude black and white film. A series of runs must be made and shot at different exposures with different calibration standards to obtain good data at such widely divergent temperatures.

3. Different lots of film and differing development procedures can have a significant effect on the results obtained. Therefore it is necessary to purchase a rather large quantity of film from the same lot and control the development process accurately. It has been found that commercial laboratories which do large amounts of development for the motion picture industry are geared to exercise the amount of processing control required. Fortunately, such laboratories are located in the Los Angeles area, so service is rapid and communications relatively easy.

4. To obtain accurate temperatures, the emissivity of the sample and the calibration standard must be known at all the temperatures of interest. More will be said about this in a later section.

5. With the lower melting temperature glasses (e.g., the gallia-calcia glass and the laser glasses), crystallization, if it occurs, happens at such a low temperature that very little radiant energy is emitted for the film to record. While useful information about nucleation and crystal growth rates could be obtained by illuminating the specimen, temperature information would be totally lacking. Shooting in a darkened room would doubtless extend downward the temperature range that could be recorded adequately. Such a procedure, however, introduces safety hazards and operational difficulties that must be evaluated carefully.

These difficulties notwithstanding, considerable progress was made during the reporting period. The alignment problems have been largely solved and suitable standard exposures for several of the higher temperature ranges of interest were determined successfully. Some tentative results were obtained with several glass compositions and are summarized later in this section. The progress made to date would not have been possible without the kind assistance of Dr. Lloyd Nelson of the Sandia Corporation, who generously shared some of his experiences in developing similar procedures for his studies.

Emissivity of Molten Oxides

There is a paucity of information in the open literature on the emissivity of oxides. The work of Dr. Noguchi and his associates at the Solar Research Laboratory, Japanese Government Research Institute (Reference 6), provides almost the only existing data for molten oxides. Dr. Noguchi has studied the freezing of many refractory oxides after solar furnace melting. He has accurately measured the emissivity at 0.65 micron, as well as the freezing points of these oxides. Some of his data are summarized in Table 2. With the single exception of zirconia, all of the oxides studied exhibited emissivities in excess of 0.90. It should be noted that all of the data obtained by Dr. Noguchi are for oxides with melting points exceeding about 1800°C. The only data on lower melting oxides was found in the Handbook of Chemistry and Physics (Reference 7) as follows:

Oxide	ε (most probable value)	Melting Point, °C
CoO	0.75	1800
SnO_2	0.32 to 0.60	1637
Copper oxide	0.70	1236
V_2O_5	0.70	675

Since there are no data on the emissivity in the liquid state of all of the oxides of interest, it is necessary to make a few assumptions before an estimate for the probable accuracy of the proposed measurements can be made. These assumptions are:

1. Mixtures of oxides will have emissivities in the liquid state no lower than that of the pure constituents.

2. Oxides of interest (i.e., Nb_2O_5, GeO_2, and MoO_3) for which we have no liquid emissivity data have liquid emissivities greater than 0.70.

Inspection of Figure 8, which is a replot of data appearing in Reference 9, shows that for emissivities greater than 0.7, temperature errors less than 60°K may be expected. At temperatures below 1500°K, emissivities as low as 0.53 should cause errors no larger than 60°K. The density of the film can

Table 2. Spectral Emissivity of Liquid Oxides*

Oxide	Freezing Point °C	Spectral Emissivity ε at .65μ (6500A°)	Oxide	Freezing Point °C	Spectral Emissivity ε at .65μ (6500A°)
Al_2O_3	2049 ± 15	0.96	Nd_2O_3	2233 ± 20	0.97
CaO	2585 ± 20	0.92	Sm_2O_3	2269 ± 20	0.98
HfO_2	2753 ± 20	0.91	Eu_2O_3	2291 ± 20	0.95
ZrO_2	2706 ± 20	0.81	Gd_2O_3	2330 ± 20	0.98
TiO_2	1833 ± 15	0.94	Tb_4O_7	2303 ± 20	0.97
Ga_2O_3	1795**	0.90-0.92***	Dy_2O_3	2228 ± 20	0.98
La_2O_3	2256 ± 20	0.92	HO_2O_3	2330 ± 20	0.98
Y_2O_3	2376 ± 20	0.96	Er_2O_3	2344 ± 20	0.94
Yb_2O_3	2335 ± 20	0.98	Tm_2O_3	2341 ± 20	0.98
Sc_2O_3	2403 ± 20	0.96	Yb_2O_3	2335 - 2355	0.98
Pr_6O_{11}	2183 ± 20	0.98	Lu_2O_3	2373 - 2427	0.93

*Reference 6
**Reference 7
***Private communication with Dr. Noguchi

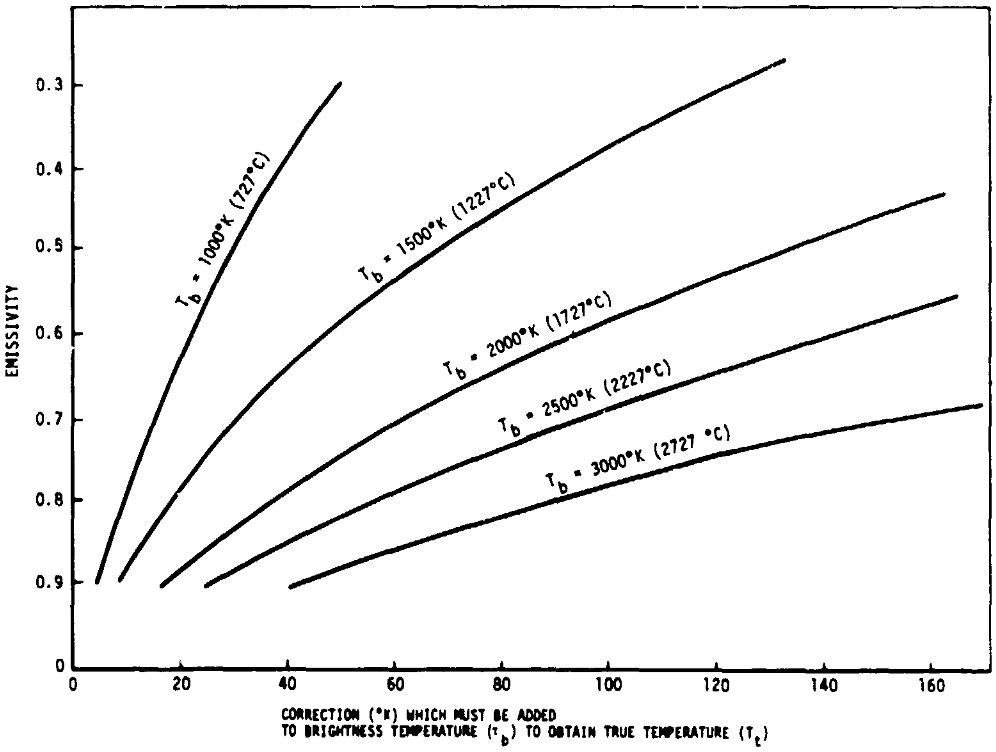


Figure 8. Temperature Corrections for Monochromatic Brightness Pyrometer Employing 65-Micron Wavelength

be read to accuracies of approximately one part in 200. Therefore errors from that source should be well within the correction error (due to emissivity unknowns). Another potential source of error is in picking off the true freezing or melting point of the temperature standard used to calibrate the film. Experience has indicated that this can be done fairly easily to within about 10°K. It would appear reasonable, then, that if a correction of 30°K were added to temperatures obtained from the film, the true temperature should be safely within ± 30°.

Temperature Standards

With the technique employed to date, at least two pure oxides with known melting points are laser melted on each lot of film. At least one of these is melted for each roll to check variations and constancy of development procedures. The oxide chosen for each roll (with a melting point within the temperature range of interest) is selected so that the film density obtained at its melting point is in the center one third of the density range obtainable for the set of exposure conditions chosen. The oxides selected for temperature standards are:

Oxide	Melting Point (°C)
Al_2O_3	2049
CoO	1800
SnO_2	1637
Nb_2O_5	1487
Cu_2O	1236
GeO_2	1116
MoO_3	795
V_2O_5	675

Hot-pressed 4-inch-long, 1/4-inch-diameter rods of each of the above oxides were ordered from the Haselden Co. Difficulty was experienced in hot pressing all but the alumina and niobia (which have been received). Recently the shape requested was changed to flat discs about 1 inch in diameter. It is anticipated that the balance of the oxides will be received in time for use in the sounding rocket program. For exploratory experimental purposes, high purity V_2O_5 was cold-pressed into a flat disc. This permitted some coverage of the entire temperature range of interest, although not in as much detail as desired.

on the film was a bit larger than the spot size, so that it was possible to obtain good readings when the sample was entirely, or nearly all molten. Good readings normally could not be obtained, for example, when the sample was approximately 50-percent molten.

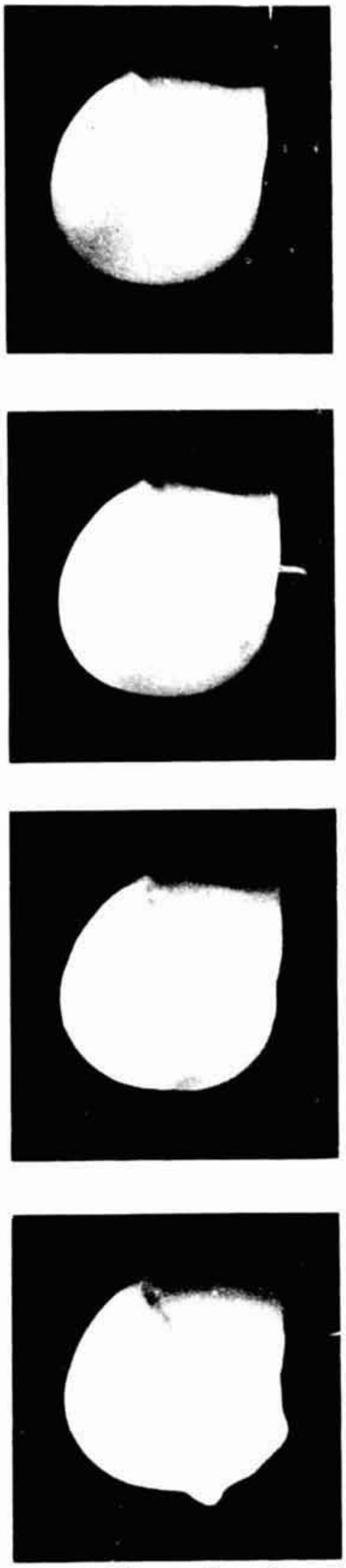
It is planned to read densities from a projected image in the future using a densitometer designed for enlarging work in photography. Such a technique should permit the reading of temperature at any point in the specimen desired. Reasonably good readings of the liquidus and solidus temperatures should be obtainable with this technique. It should also be possible to determine the amount of undercooling occurring in samples that crystallize on cooling.

Particular difficulty was experienced in obtaining good readings on the alumina and niobia temperature standards. Usually the size, as recorded on the film, of the molten pool formed on the end of the rod was less than the densitometer spot size. However, it was possible to obtain a small number of good readings so that a first approximation of the superheating temperature was obtained. These results are summarized as follows:

Composition	Maximum (superheat) Temperature, °C	Approximate Time to Reach Max. Temperature, sec.
40 CaO lasing glass	1750 - 2160	5 to 7
Gallia - 20 calcia	1800 - 2180	4 to 9
Alumina - 40 lanthana - 20 calcia	2160 - 2200	5 to 9
Alumina - 30 calcia	2160 - 2200	10 to 11

These values represent the range obtained for a number of different runs. It should be noted that some runs of each material approached 2200°C. Therefore it would appear that a given size sample quickly reaches a temperature equilibrium that represents a state in which the power input from the laser equals the energy lost by radiation and conduction to the supporting air stream. It is apparent that the only way to reduce the temperature achieved is to reduce the power of the laser beam. This was done in experiments with the lasing glass, the results of which are reported earlier.

Selected portions of scenes from the motion pictures obtained have been assembled into a short movie which has been shown to interested NASA, academic, and industry personnel. Selected frames from that movie are reproduced as Figures 9 through 14. They highlight some of the more interesting events observed in the films.



a. Frame 582 (0 sec)

b. Frame 599 (0.27 sec)

c. Frame 609 (0.31 sec)

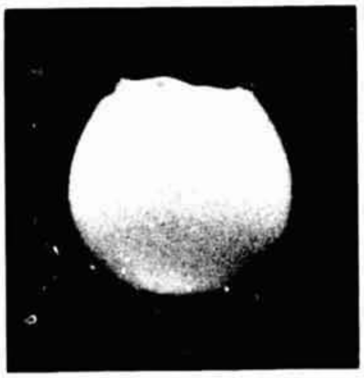
d. Frame 617 (0.55 sec)

Figure 9. Crystallization of 40 La_2O_3 - 40 Al_2O_3 - 20 CaO

a. Frame 2002 (0 sec)

Melting--Liquid + undissolved, crystalline solid

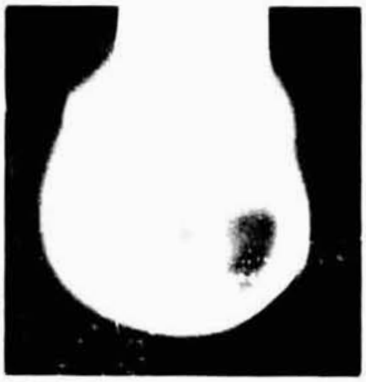
Laser beam coming from left, rear



b. Frame 2346 (5.4 sec)

Cooling (glass)

Figure 10. Glass Formation with 40 La_2O_3 - 40 Al_2O_3 - 20 CaO



a. Frame 1038 (0 sec)

Melting
Liquid + undissolved, crystalline solid.

Laser beam coming from left-rear

b. Frame 1374 (5.6 sec)

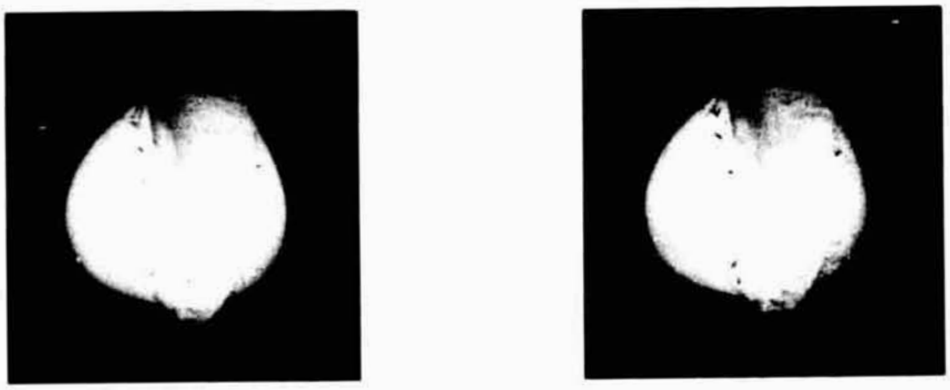
Cooling (glass)

c. Frame 1421 (6.0 sec)

Cooling (glass)

Figure 11. Glass Formation With 40 La_2O_3 - 40 Al_2O_3 - 20 CaO

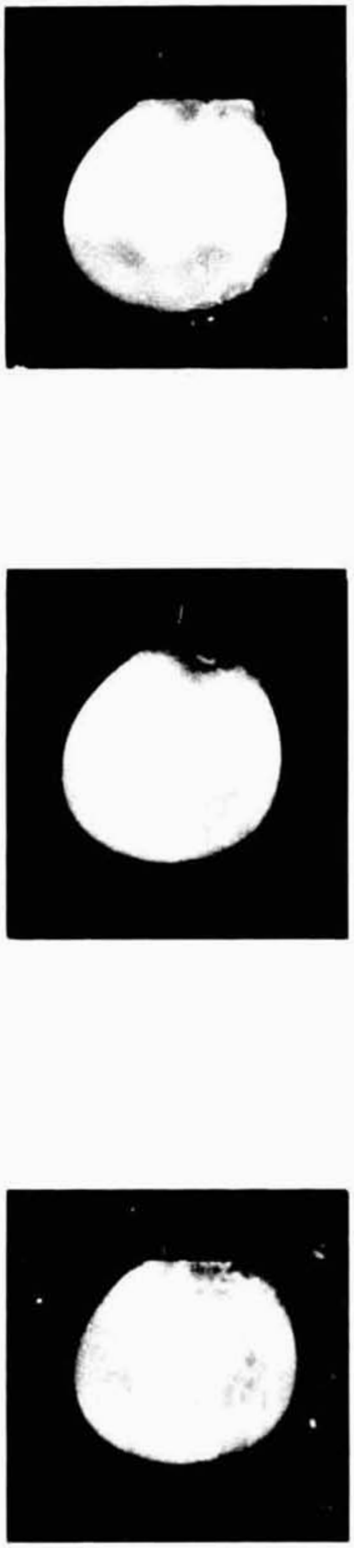
a. Frame 3630--Glass With Bubbles



b. Frame 4815 (0 sec)

c. Frame 4874 (0.9 sec)

Figure 12. Glass Formation With 70 Al_2O_3 - 30 CaO

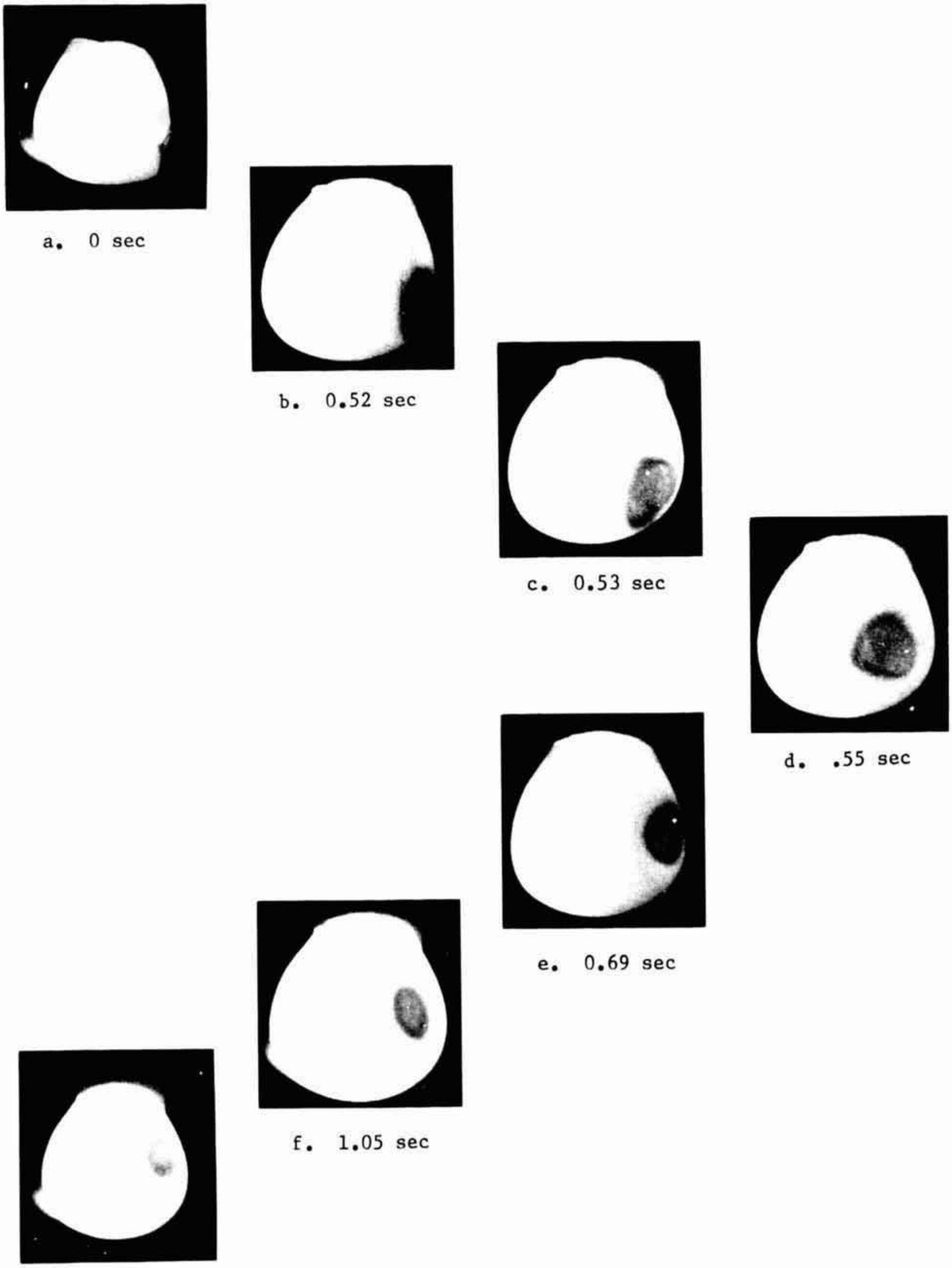


a. Frame 7825 (0 sec)

b. Frame 7832 (0.11 sec)

c. Frame 7936 (1.7 sec)

Figure 13. 40 CaO Laser Glass



a. 0 sec

b. 0.52 sec

c. 0.53 sec

d. .55 sec

e. 0.69 sec

f. 1.05 sec

g. 1.06 sec

Figure 14. 80 Ga_2O_3 - 20 CaO Showing Turbulence During Melting

The four frames selected for Figure 9 show the progress of a crystal growth front which starts at the top of the sample and proceeds downward. As can be seen from the times shown on the figure, the crystal grows quite rapidly, taking slightly over 1 second to consume the entire melt. The bottom frame is interesting in that the crystal front actually grew past the confines of the liquid from which it formed, leaving a spike on the surface.

Figure 10, also of the ternary lanthana-alumina-calcia composition, shows in the upper frame the appearance just before a 100-percent molten state is reached. Note the boiling occurring at the upper left part of the sample and the unmelted portion which shows up as a darker zone to the right of the vertical center line. In the lower frame is shown the cooling glass. It is relatively featureless, as might be expected. The bottom portion is darker, indicating that it is cooler. This probably represents extra cooling resulting from the impinging air stream from the wind tunnel. It should also be noted that the probe itself is invisible in this frame, an indication that it is at a much lower temperature than the cooling melt. The reader should be cautioned against attempting to draw any inferences about temperature by comparing one frame with another in this or any of the other sequences shown here. These are prints from the original negative prepared in Rockwell's production printing shop. Therefore, the printing exposure was varied in order to produce a good-appearing print.

Figure 11, also of the ternary glass, shows frames from another run that resulted in glass formation. The top frame shows melting and the lower two frames show the cooling glass. These two frames are illustrative of the point made in the preceding paragraph and show similar overall densities in the print in spite of the fact that the lower frame is significantly cooler than the center one. The lower frame shows the outline of the partially dissolved silica probe and is illustrative of the climbing effect noted when the air velocity from the tunnel is too high or the superheat temperature excessive.

Figure 12 shows glass formation with two runs of the 70/30 alumina-calcia composition. Many bubbles can be ssen. Both climbed the probe, but not symmetrically. In the run of Figure 12a, the climbing is up and to the left. In Figure 12b and 12c, the climbing is up and away from the camera. The partially dissolved probe can be seen clearly in the latter two prints.

Figure 13 shows frames from one melting sequence of the 40 m/o calcia lasing glass. Note that in the upper frame, large bubbles can be seen at the four to five o'clock position near the surface. The bubbles appear to be gone in the central frame and reappear in the bottom frame. It is felt that the apparent disappearance of the bubbles may be associated with the optical characteristics of the material at elevated temperatures. The material appears to be opaque at 0.66 micron at a temperature range achieved in the center frame. The absorption band has apparently swept to another wavelength in the bottom frame and the material is again transparent at 0.66 μ.

The frames selected for Figure 14 show the gallia-calcia glass as it is being melted. Note that the dark, unmelted, portion changes position rapidly from frame to frame. Observation of the movie shows clearly that the unmelted portion is swirling rapidly, indicating there is strong turbulence within the melt as it is being melted. The reason the boiling from the impinging laser beam cannot be seen in Frames b through e is that the laser used is of the alternating current type and those frames happened to be shot during the off portion of the cycle.

Discussion of Progress to Date

It is felt that the major hurdles have been overcome in development of a viable cinematography technique for studying the air suspension/laser melting process in detail. The alignment and exposure problems have been solved and the temperatures determined to date have been sufficiently accurate to enable us to glean valuable information from the motion pictures. Several areas need further work. These are summarized in the following paragraphs.

Densitometer techniques need improvement. It is felt that reading densities of the negative from a projected image will enable fast, accurate measurements to be made in any portion of the sample desired. It is anticipated that a suitable densitiometer to enable this to be done will be purchased on the sounding rocket program. As a backup, there is a microdensitometer available at the Rockwell Science Center in Thousand Oaks, California. We are reluctant to use it, however, because the measurements are time-consuming and the location is relatively remote from where the bulk of the work will be done.

More temperature standards are needed, especially at temperatures below 1500°C. It is hoped that the complete series of hot-pressed rods, hopefully to be received shortly, will fill in the gaps that presently exist. Better emissivity data, especially in the liquid state just above the crystalline melting temperature of the lower melting point pure oxides, would be most helpful in improving confidence in the temperatures determined. It is not proposed to do such work on this program in the near future, however, because of funding and manpower limitations.

It would be desireable to obtain film in rolls greater than 125 feet in length. This is the standard length supplied by Eastman Kodak for the Shellburst film. Inquiries are being made about obtaining 500-foot rolls on special order. If the minimum quantities required are not too large, the availability of longer rolls will considerably reduce the footage consumed for calibration (with temperature standards) and should permit studies of longer cycles. This may become especially important as we get more into preparing glass samples using lower superheat temperatures than have been used in the past.

SOUNDING ROCKET EXPERIMENT STUDIES

During the reporting period some work was done to support a probe (or sting) positioning approach for sounding rocket experiments. It was felt by NASA that the G forces within the sounding rockets during the coasting phase of the flights would be too high to permit a free-floating sample during the melting and cooling portions of the glass preparation cycle. NASA personnel also expressed the opinion that acoustic positioning development had not progressed far enough (as of the summer of 1975) to permit scheduling of early flights with the gallia-calcia glass. The reason for the hesitancy on NASA's part was the tie-in of sonic positioning with a furnace capable of heating gallia-calcia melts to the temperature range, 1550 to 1600°C in air.

Probe Experiments

In response to this information, it was decided to propose to NASA an approach in which positioning was achieved by means of a silica probe, along the lines of the terrestrial research with the vertical wind tunnel. There appeared to be little doubt that the wetting forces between the sample and the probe would be more than adequate to cope with the small g forces in the sounding rocket. The principal concern is that in a near-zero-gravity field the sample may creep along the probe, being driven by wetting forces, and the end result may be a sample with the probe completely embedded through a diameter. Such a condition would undoubtably cause the sample to shatter on cooling because of differential thermal contraction between the sample and the silica probe.

There appeared to be two approaches to preventing probe embedment:

1. Use two probes on the same axis with the sample suspended between them. Surface tension forces would then be opposite and equal and movement along either probe prevented.[1]
2. Use vitreous carbon as a "stop-off" material. This is discussed in more detail later in this section.

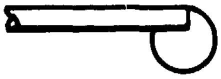
Some cursory experiments were performed in an attempt to determine whether creep along the probe was a real problem and also whether the use of two probes would, indeed, solve the problem. Samples of both gallia--20 w/o calcia and alumina--30 w/o calcia were puddled onto the end of some silica probes, in the same manner used for performing the air suspension melting. In the experiments performed in this case the probe was chucked in a horizontal position over the wind tunnel exit and the glob of oxide melted with the laser beam. Numerous attempts were made to adjust the air stream velocity to hold the molten sample opposite the end of the probe as follows:

---

[1] Unless the ends of the probes were separated by less than one melt diameter, in which case partial embedment could result as the surface tension forces caused the sample to assume a spherical shape.

In each case the sample ended up distributed along the end portion of the probe, as follows:

or



It was difficult to determine whether creeping was the reason or, alternatively, whether the final position resulted from unbalanced forces because of the difficulty of adjusting the air velocity to obtain a true equilibrium position in line with the probe. Next, a second, handheld probe was touched to the melt and a liquid pool was formed between the two probes. It was found possible to move the hand-held probe in and out and change the length and diameter of the suspended liquid significantly, as follows:

and

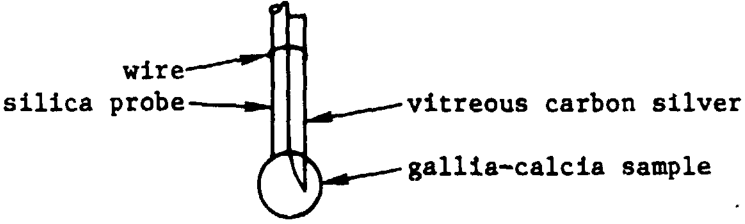
There appeared to be no tendency for the sample to surround either probe. If the movable probe were withdrawn to the point that the melt fractured it invariably hopped back onto one of the probes in the following manner:

The conclusion that may be drawn from these experiments is that the two-probe approach appears effective in preventing creep or embedment of the sample. It was not possible to determine conclusively whether embedment would be a real problem in zero gravity. However, it appeared that such probably would be the case.

Some samples of "vitreous" carbon were obtained from a supplier, the Beckwith Carbon Corporation of Van Nuys, California. Vitreous carbon is prepared by the thermal degradation of certain organic polymers, such as phenolics. It is termed "vitreous" because of its glossy (black) appearance and its conchoidal fracture. It is not truly a glass but appears to have a "turbostratic" structure consisting mainly of graphite-like hexagonal layers in very small "packets", with no true graphite orientation between the layers. The crystallite size appears to be a decade or more smaller than that for a typical electrode graphite.

Several experiments were performed to determine whether vitreous carbon would prove to be a suitable material for preventing creep of glass melts in zero gravity. The first experiment consisted of attempting to melt samples of the 35 m/o CaO lasing glass on a flat slab of vitreous carbon. The first six or seven attempts resulted in crystalline material. There appeared to be absolutely no wetting of the carbon by the lasing glass candidate composition, however. Finally, a smaller sample was melted and a glass sample was produced. Half of this sample was sent to Owens-Illinois who confirmed it was 100-percent glassy. There are alternative explanations for the failure of the earlier attempts to yield glass. The most plausible explanation to the writer, is that the sample was too large, coupled with a heat sink effect from the carbon slab so that it was not possible to heat the entire sample above the liquidus. The possibility that the vitreous carbon nucleated the material on cooling cannot be conclusively ruled out, however.

Attempts to prepare gallia-calcia glasses on the vitreous carbon slab were inconclusive because the material skipped off the slab as soon as it was melted. No better results were obtained when attempts were made to melt the material on the concave surface of a piece of broken vitreous carbon tubing. Finally, a sliver of vitreous carbon was wired to the side of a probe and a glass sample was prepared. This setup was as follows:



With this experiment the vitreous carbon projected well into the molten gallia-calcia glass sample. This experiment tends to confirm the earlier results with the laser glass that vitreous carbon may not nucleate the glasses on cooling. Further experiments will be to be performed, however, before confidence can be obtained in vitreous carbon as a potential stopoff material.

Equipment Design Study

A study was instituted, using Rockwell internal funding, to design equipment for incorporating the probe approach into an ARTCOR ceramic element furnace. The basic approach of this design involved the positioning of two samples inside the furnace cavity with silica probes. Vitreous carbon tubes surrounded the probes to prevent creep along the probes. The design also permitted the use of two probes with one sample in the event that further experiments that were to be performed during the course of the sounding rocket program demonstrated that the use of vitreous carbon was too risky. Proprietary features were also included to support the samples during liftoff and to permit rapid cooling after the samples were melted and superheated.

As of this writing the ARTCOR furnace will not be used on the first few flights. NASA has decided to pursue acoustic positioning with a high-temperature furnace, instead.

FUTURE GROUND-BASED WORK REQUIRED TO SUPPORT SOUNDING ROCKET EXPERIMENTS

It seems appropriate to point out that, as of the time of the preparation of this report, terrestrial research work required to support future sounding rocket flights is, effectively, being terminated by NASA. While the writer expects to participate in two early sounding rocket flights, available funding permits only the minimum work required to support directly those two flights.

The first two flights are scheduled to attempt to prepare one half-inch diameter spheres of glass from the gallia-20 w/o calcia and alumina-30 w/o calcia compositions.

No work is scheduled to continue the work on lasing glasses. Work that needs to be done at an early date includes:

1. Further experimental work to determine a suitable starting material. One such possibility is hot pressing.

2. Owens-Illinois has been developing lithia-free laser glass candidate compositions in response to the high lithia losses encountered in the containerless laser melting experiments performed to date. These compositions need to be evaluated in the containerless laser melting setup. Such an evaluation should include cinematographic studies as well as liquidus temperature determinations.

3. Further work is required to minimize silica pickup during terrestrial preparation. Possibilities for accomplishing this include:

    a. Reducing the superheat temperature and measuring the temperatures actually achieved using cinematography techniques.

    b. Performing experiments with a 1-g acoustic levitation unit without the use of silica probes. The CO_2 laser could conviently be used to melt the samples. Such an approach should also permit the evaluation of different melting atmosphere compositions, such as air, oxygen, and inert gasses such as argon.

It is felt that the laser glasses may represent some of the most saleable potential accomplishments of the NASA space processing activity. Since they generally have low melting points, their preparation in sounding rocket experiments should pose simpler equipment problems than is the case with the optical glass candidate compositions, many of which have liquidus temperatures exceeding 1700 C.

REFERENCES

1. Happe, R. A., Manufacturing Unique Glasses in Space - First Interim Report. Rockwell International Corporation, Space Division, SD 74-SA-0174 (November 1974).

2. Poor, W. S., Measurements and Tests of Special Glass Samples. Perkin Elmer Corporation, Optical Group Engineering Report 12571 (August 1975).

3. Jenkins and White, Fundamentals of Optics. New York: McGraw-Hill (1957), p. 469.

4. Brewster, G., J. R. Hensler, J. L. Road, and R. A. Weidel, "Partial Dispersion Ratios of Some New Borate and Phosphate Glasses," Applied Optics 5, 12 (1966), p. 1891.

5. Neilson, G. F., and M. C. Weinberg, Development of Improved Amorphous Materials for Laser Systems. Owens-Illinois, Inc., Final Report, Task Order RD-151, Contract 953846 under Contract NAS7-100 (November 1974).

6. Noguchi, T., et al, Solar Energy. Vol. 10, No. 3 (1966), Vol. 11, No. 1, 2, 3, and 4 (1967).

7. Handbook of Chemistry and Physics. 5th Edition, Langley Research Center.

8. Phase Diagrams for Ceramists. American Ceramic Society (1964).

9. Herzfeld, C. N., Temperature, Its Measurements and Control in Science and Industry. Part 1, Section IX (Article by G. O. Nutter (1962), p. 537.