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MASS SPECTROMETER ANALYSES OF BUBBLES IN FLUORIDE
GLASSES(U) BROCKWAY INTERNATIONAL PA J E FENSTERMACHER
17 JUN 87 E1230 N00044-86-C-2405

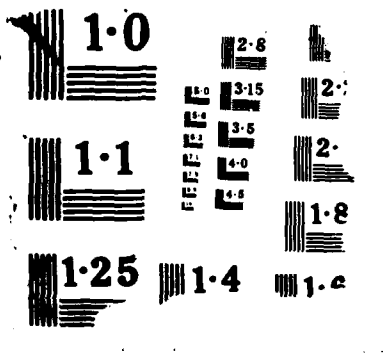
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Fenstermacher, James Edward

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Fluorozirconate glasses
Low-loss optical fibers
(see reverse)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

These reports contain accomplishments, interim results, conclusions, trends, and delays in relation to the characterization of gas bubbles in fluorozirconate fiber optic preforms.

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→ Gas bubbles in preforms and fiber
mass spectrometer analyses ↗

Fenstermacher to Busse
Report No. BNRL/3 - BNRL/7
Contract No. N00014-86-C2405
Naval Research Laboratory

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BNRL/6	Monthly Progress Report for April '87 (1p.)
BNRL/7	Monthly Progress Report for May '87 (2 p., 1 table, 2 p. notes) Lot 4 analyses

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Brockway

February 17, 1987

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, D.C. 20375-5000

ATTENTION: Dr. Lynda Busse, Code 6570
Report No. BNRL/3

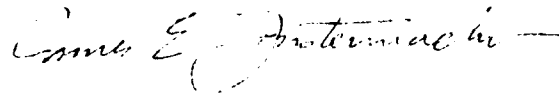
Dear Dr. Busse:

This report notes the activity on Contract N00014-86-C2405 for December 1986 and January 1987.

Report No. BNRL/2 describing our results on the first two sets of samples you supplied for analysis was mailed December 17. Per our telephone conversation on January 13, you will be getting back in touch with me to review the first set of analyses.

No further sample lots have been submitted since the first two noted above. If appropriate, it would be well to send us several sets of samples and a priority listing. Sample preparation is time consuming and our own workload unpredictable (primarily production problem-solving). Therefore, having a quantity of samples on hand would enable effective scheduling of analyses in the time remaining on the contract.

Very truly yours,
BROCKWAY, INC. (NY)



James E. Fenstermacher
Physical Chemistry Group
Research and Development

JEF:jlh

cc: ACO/DCASMA
Dir. NRL
DTIC
I. Munn
T. Kalgren

Brockway

March 20, 1987

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5000

ATTN: Dr. Lynda Busse, Code 6570
Report No. BNRL/4

Dear Dr. Busse:

This report notes activity on Contract N00014-86-C2405 for February 1987.

We received the samples described in your letter of February 26, 1987 (SER 6570/88) on March 4. The samples consisted of one nominal 3 mm cube of bulk glass labeled ZF1703 and three preforms labeled B82, B100, and B135. All three preforms contain many bubbles whose diameters range up to 3 or 4 mm strung along the axis of the preforms. As we discussed by phone on March 10, we will select 3 samples from each preform - one each from either end of the string and the third from the middle. We are slicing up the entire preform and will have a variety of samples for further analyses if you desire.

As reported in our discussion, we have had some problems with fracturing of the preform during cutting, particularly near some of the larger bubbles. We are using a 4 inch diameter, .012 inch wide blade on our Isomet and running at speed settings between 6 and 7. Loading the samples lightly seems to help but it does increase the time required to cut the samples out. We intend to load samples from the three preforms sometime next week and analyze them all on the same day. Some of the bubbles that fractured very quickly drew in the cutting fluid leaving no apparent trapped bubbles of gas. On this basis, I expect these will be low pressure samples and intend to use the largest intact bubbles we can isolate.

Dr. Lynda Busse
March 20, 1987
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This report was delayed slightly to report the following. We have analyzed the bulk sample Grant Lu submitted. Sample ZF1703 contained several dozen bubbles of diameters ranging from .01 to .05 millimeter (10-50 microns). A single 50 micron bubble at 33 kilo pascals (1/3 atmosphere) internal pressure would yield approximately 2×10^{-6} pascal liters of gas. We observed in two successive fractures of the sample approximately 10×10^{-6} and 5×10^{-6} pascal liters of pure argon. No other significant species were observed. These bubbles are apparently at a fairly high internal pressure, i.e. 100 kilo pascals. As an aside, the quantities of argon were large enough that we observed a significant Ar 36 peak (~ 0.36% of the parent Ar 40).

The effective date of Contract N00014-86-C2405 is September 3, 1986. Section F-1 of the contract specifies that the period of performance for the contract is 9 months i.e. the work is to be completed by June 3, 1987. The contract also calls for analyses of 35 sample "sets" of which only 3 have so far been submitted. It seems very likely that an extension of the contract will be necessary in order to complete the specified series of analyses. I have discussed this matter with Richard Heraty, our manager of Business Development, and we feel that Brockway and NRL should address the necessity for such an extension now. We would appreciate your attention to the question of an extension and your input regarding the appropriate action to be taken on our part.

Yours truly,



James E. Fenstermacher
Physical Chemistry
Research and Development

JEF/jr

cc: ACO/DCASMA
Director NRL
DTIC
D. Heraty
I. Munn
T. Kalgren

Brockway

April 15, 1987

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5000

ATTN: Dr. Lynda Busse, Code 6570
Report No. BNRL/5

Dear Dr. Busse:

This report presents the following activity on Contract N00014-86-C2405 for March 1987. The analyses presented herein confirm the results I reported by phone on April 2.

The samples accompanying your letter of February 26, 1987 (SER6570/088) were received March 4 and consisted of 3 preforms - B82, B100 and B135 - and one bulk sample - ZF1703. In our phone conversation on March 9 we agreed to consider the samples as a single lot (Lot 3) and analyze the bulk sample and samples from the ends and the middle of each preform.

The analysis of the bulk sample (10-50 micron diameter bubbles yielding Argon at high pressure) was reported last month (Report No. BNRL/4). The enclosed results on the preforms indicate, as with the Lot 1 & 2 analyses, that the bubble-forming gases have gone back into solution leaving in only two cases traces of Argon - both in samples from B135.

Increases in CO_2 were observed on breaking the fluoride preforms in the system. As described more fully in the attached discussion, I feel this is a desorption phenomenon but have suggested an experiment involving sodium-containing and sodium-free fluoride glasses that may help resolve the question.

Fracture of the preforms is a problem. As noted in the discussion, in order to avoid further loss of intact samples we attempted no further machining of the samples after they were sliced from the preforms. In the future

Fenstermacher to Busse
Report No. BNRL/5
April 15, 1987
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I leave it to your discretion to supply us with the preforms or samples cut to size. The 8-station holder can accommodate 12-13 millimeter diameter samples a few millimeters thick - the 21-station holder, 5-6 millimeter cubes or 7 millimeter diameter samples up to 5 millimeters thick.

In last month's report, I raised the question about the necessity to arrange an extension on the contract. This is only the third of the 35 sets of analyses contracted for with less than two months left - also as specified in the contract. Considering the time available this is a matter that should be addressed immediately.

Yours truly,



J. E. Fenstermacher
Physical Chemistry
Research and Development

JEF/jr

Attachment

cc: ACO/DSASMA
Director NRL
DTIC
D. Heraty
I. Munn
T. Kalgren

enstermacher to Busse
 Report No. BNRL/5
 April 15, 1987

Table I - Lot 3 Analyses

<u>Preform</u>	<u>Sample Code & Location</u> (See Note 1)		<u>(Number) of Bubbles</u> & <u>Vol. (microliter)</u>		<u>Observed</u> <u>Gases</u> (See Note 2)	<u>Observed</u> <u>Pressure</u> (pascal)
B82	C	9.3 cm	(1)	0.008	NSD	--
	N	4.4 cm	(1)	0.23	NSD	--
			(3)	0.035	NSD	--
B135	A	11.0 cm	(1)	0.0007	Ar	< 800
			(2)	0.0001		
	J	7.6 cm	(1)	0.37	Ar	< 1
(2)			0.11			
	P	4.3 cm	(1)	0.57	NSD	--
B100	B	3.2 cm	(1)	5.6	NSD	--
	F	5.5 cm	(1)	0.51	NSD	--
	M	7.3 cm	(1)	0.25	NSD	--
(1)			0.23			
(1)			0.054			

Fenstermacher to Busse
Report No. BNRL/5
April 15, 1987

Discussion & Notes Concerning the Data of Table I

Note 1 - All three preforms contained bubbles of sizes ranging up to several millimeters in diameter. All the bubbles were strung out along the axis of the preforms. Each sample was mounted on our Isomet and successive slices - coded A, B, C. etc. - were cut from the preforms attempting to isolate individual bubbles if possible. "Location" is the distance of each slice from the rounded end (bottom?) of the preform. In most cases there were a number of smaller bubbles scattered in the area immediately adjacent to the "target" bubble. Those samples containing a minimum number of bubbles and nominally from the ends and middle of the string were selected for analysis. Many samples - particularly the largest - broke as the saw blade cut past the axis of the preform along which the bubbles are located. In all cases, the cutting fluid was observed to be drawn immediately into the bubble volume leaving no apparent gas bubble behind. To prevent further loss of samples we loaded the nominal 12, 13 millimeter discs cut from the preform in our 8-station sample holder to eliminate the need for any further machining.

Fenstermacher to Busse
Report No. BNRL/5
April 15, 1987

Discussion and Notes
Page 2

Note 2 - All samples were broken twice - the first time as gently as possible, the second time to insure that the bubbles were broken open. In most cases NSD - nothing significant detected over existing MS background - was observed. (See also Note 2 in Report No. BNRL/2, December 15, 1986). In two cases, both on preform B135 samples, Argon was observed (on the initial attempt). Internal pressures (See Note 1 in Report No. BNRL/2) were calculated assuming that the Argon was present in the largest bubble. Even in the extreme case, B135A, low bubble internal pressures are observed - less than 1/100 atmosphere.

All samples were analyzed on March 27 - no other glass was present in the system. As I have described previously, fresh fracture surfaces of soda-lime silicate glasses readily absorb gases like CO_2 , H_2O , and SO_2 . As we have seen so far, the fluoride glasses you have submitted do not. During the course of the day we observed what we would ordinarily consider significant increases in CO_2 when the samples are broken. Note 3 in Report BNRL/2 cited observation of CO_2 (and N_2) on the order of 3 or 4 times the nominal minimum detectability for CO_2 . It was also noted that the phenomenon was not observed each time samples were broken or recrushed. In the current series, quantities ranging from 2 to 20 times the CO_2

Fenstermacher to Busse
Report No. BNRL/5
April 15, 1987

Discussion and Notes
Page 3

"minimum" were noted on all samples - on the initial break and on the recrush including the single-bubble samples. The quantities of CO_2 involved are not apparently related to bubble size. I believe the gas is most likely desorbed from the system walls when the samples are broken. There is, however, the possibility that the CO_2 could be released from the glass. While there is evidence in the literature for CO_2 dissolved in fluoride glasses, much higher levels are present in the soda-lime silicates. My experience with the latter says that only gases physically dissolved in the glass can be released in this manner. If you are interested in pursuing the matter further, I would suggest a series of analyses comparing the results of crushing Na-containing and Na-free fluoride glasses. The former, while potentially containing more dissolved CO_2 should yield little or no CO_2 when broken and also gradually reduce the amount of "desorbable" CO_2 in the system.

In summary, the analyses indicate that the gas(es) originally forming the bubbles have gone back into solution. The data of Mathew and Doremus (J. Am. Cer. Soc. 70 C86-C89 (1987)) show that likely candidates are F_2 , HF and Zr fluorides. No indication of fluoride species has been seen in any of our analyses to date.


James E. Fenstermacher

Brockway

May 15, 1987

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-500

ATTN: Dr. Lynda Busse, Code 6570
Report No. BNRL/6

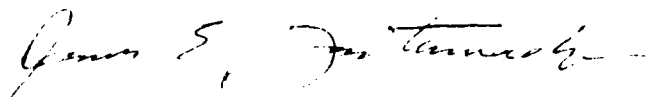
Dear Dr. Busse,

This report presents the following activity on Contract
N00014-86-C2405 for April 1987.

No samples were submitted for analysis during April. As I have noted in previous reports and as we have discussed most recently on April 28, the contract called for 35 sets of analyses to be performed within a 9 month period beginning September 3, 1986. It appears that, following receipt and analysis of the samples we discussed briefly on May 12, no further samples will be submitted - well short of the 35 originally called for in the contract.

As we discussed today, the final set of analyses will consist of 2 groups of three bubbles from the 2 preforms being sent to us. The 3 bubbles will be taken from the ends and middle of each preform. We will also analyze at least two samples from one of the three B-series glasses submitted in March using our low mass magnet - primarily to look for the presence of H_2 . All previous analyses were performed using the high mass magnet which allowed scanning the mass range 12-100⁺ thereby "missing" H_2 , He, and Ne. Although none of these gases is expected to be found, the analyses will be performed primarily to confirm that H_2 - within our ability to detect it - is not present in the bubbles.

Yours truly,



James E. Fenstermacher
Physical Chemistry
Research and Development

JEF/pm

cc: ACO/DCASMA
Director NRL
DTIC
D. Heraty
I. Munn
T. Kalgren

Brockway

June 17, 1987

Naval Research Laboratory
4555 Overlook Avenue, S.W.
Washington, D.C. 20375-5000

Attn: Dr. Lynda Busse, Code 6573
Report BNRL/7

Dear Dr. Busse:

This report presents the following activity on Contract N00014-86-C2405 for May 1987. The analyses presented confirm the results I reported to you by phone on May 28. The latest samples were submitted along with your letter of May 12, 1987 and are the last samples submitted within the 9-month period of performance as specified in the contract (effective date - September 3, 1986).

The samples noted above were received May 18 and consisted of two fluoride glass rods labelled RR4 and RR13. As in the past, analysis of samples from the top, middle, and bottom of the rods were required. Prior to receiving the samples, we had discussed (May 15) my concern that, although H₂ was not expected to be involved in the bubbles-in-fluoride glass problem, we had not positively confirmed that H₂ (or any other species with mass peaks below AMU 12) was not present. We agreed that samples from a previous lot which yielded little or no detectable gases would be analyzed especially for the presence of low-mass species. As noted in our report BNRL/6 (May 15), the low-mass analyses would be incorporated with analyses of the RR samples and considered as a single lot (Lot 4).

All samples were loaded as a group and analyzed on May 28. The low mass analyses were done on samples from Lot 3 (see report No. BNRL/5). No significant increases in H₂ or any other low mass species were seen during our analyses which included an initial break and a second "recrush" to insure that the sample was broken.

Table 1 presents the results of the Lot 4 analyses. Only the largest sample from RR13 yielded any appreciable quantities of gas -- both CO₂ and Ar with no question of their presence in the sample. Even at that, the calculated internal pressure of

Naval Research Laboratory
June 17, 1987
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that bubble is very low (~ 30 pascal). Analyses of smaller RR13 samples (0.31 and .020 microliter) yielded apparently significant increases in argon over background. Since argon was noted on both the initial and subsequent recrush of the smallest single bubble sample, the possibility exists that Ar may have been released from physical solution in the glass rather than from the bubbles in the glass. These two pieces of glass were close to the top of the preform whereas the larger bubbles came from the bottom. The quantity of gas observed in the 5.5 microliter sample is ~ 200 times greater than that observed on crushing the two "top" bubbles. No significant argon was noted on analysis of the RR4 samples regardless of position.

The above is meant only to bring the possibility of physical solution to your attention. Further speculation on my part is not worthwhile in the absence of the preparation (melting history) of these and other glasses that you have submitted for analyses.

As noted earlier, these are the last analyses that will be performed under the terms of Contract N00014-86-C2405. As specified in the contract, a final report summarizing our work for NRL will be submitted within 60 days of the close (June 3) of the contract. If you have any further questions, comments, or information that may have a bearing on that report, please convey them to me as soon as possible.

Yours very truly,



James E. Fenstermacher
Physical Chemistry Group
Research and Development

JEF/nw

cc: ACO/DCASMA
Director NRL
D. Heraty
I. Munn
T. Kalgren

Fenstermacher to Busse
 Report No. BNRL/7
 June 17, 1987

Table I - Lot 4 Analyses

<u>Preform</u>	<u>Sample Location (see Note 1)</u>	<u>(Number) of Bubbles and Volume (microliter)</u>		<u>Observed Gases (See Note 2)</u>	<u>Observed Pressure (Pascal)</u>
B82	10.2 cm	(1)	0.003	NSD*	--
B100	5.8 cm	(1)	0.42	NSD*	--
B135	8.0 cm	(1)	0.028	NSD*	--
RR4	2.0 cm	(1)	2.4	NSD	--
	5.0 cm	(1)	0.078	NSD	--
	7.9 cm	(4)	0.087 (Total)	NSD	--
	8.1 cm	(1)	0.29	NSD	--
RR13	1.5 cm	(1)	5.6	67% Ar, 33% CO ₂	30
	5.9 cm	(1)	1.1	NSD	--
	6.5 cm	(1)	0.31	Ar**	0.1
	7.3 cm	(1)	0.020	Ar**	5

* "low mass" analyses (See Note 3)

** see Note 4

Fenstermacher to Busse
Report No. BNRL/7
June 17, 1987

Discussion and Notes Concerning The Data of Table 1

Note 1 As in Report BNRL/5, "Location" is the nominal distance of each sample from the rounded end (bottom?) of the preform. Samples were selected to represent "top", "middle", and "bottom" of the bubble string in each sample and when possible, to isolate the largest single bubble in that area. No problems were noted in slicing the samples on our Isomet.

Note 2 Also as in Note 2 Report BNRL/5, all samples were broken twice - the first time gently, the second to insure that the bubbles were broken. In only one case (RR13, the 0.020 microliter sample) did two analysis "breaks" on the same sample yield a significant quantity of gas (argon) over background (see Note 4). With the exception of the 5.6 microliter sample, no variation in CO₂ background or desorption phenomena as noted in previous reports was seen. In the case of the 5.6 microliter sample, the quantity of CO₂ observed was well above our minimum detectable level and it was undoubtedly present in the sample along with the argon.

Note 3 During "low mass" analyses the mass range starts at AMU2 rather than 12. This is used to determine H₂, He, Ne primarily. Higher mass data is also obtained but attenuated considerably by comparison to our normal "high mass" analysis.

Fenstermacher to Busse
Report No. BNRL/7
June 17, 1987
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Note 4 As noted in the body of the report, the observation of argon on both breaks of the 0.02 microliter RR13 sample raises speculation that this is the release of physically dissolved argon. The bubble pressure cited assumes the argon to have been present in the bubble. If so, the internal bubble pressure are (consistently) very low.

END

DATED

FILM

8-88

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