SYNTHESIS REPORT

FOR PUBLICATION

DEVELOPMENT OF THE GAS FILM LEVITATION (GFL) TECHNIQUE TO PRODUCE HIGH QUALITY STRUCTURAL AND OPTICAL GLASSES.

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PARTNERS :	SOCIETA ITALIANA VETRO CEA-CEREM UNIVERSITY OF CLAUSTHAL UNIVERSITY OF SUSSEX

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1. Summary

1.1 Keywords

Gas film levitation technique, Containerless processing, Sodalime glass, Fluoride glass, Glass homogeneity

1.2 Abstract

The present project was articulated about the development of the Gas Film Levitation (GFL) technique applied to the preparation of two glasses of industrial relevance. One glass family was an oxide sodalime (SLS) float glass (flat glass used in the car and building industries] in order to improve the surface properties (mechanical strength, coating adhesion); the other glass family was a fluoride glass, known as ZBLAN, which had considerable potential for the preparation of ultra low loss optical fibres at 2.55 µm wavelength. This last glass family was studied to improve its bulk properties {scattering loss, homogeneity).

The GFL technique has been successfully applied to the preparation of reference samples of model and industrial product SLS (oxide) glasses from precursor disks and many SLS discs have been prepared by this process at high temperatures {up to 1450°C}. up-grading of the levitation facility has allowed contactless processing of large SLS glass samples (Φ 80 mm, 160 g) which corresponds to an improvement of an order of magnitude in weight for the levitation technique. The development of a prototype to levitate large float glass plates was not found to be industrially relevant but a flotation technique derived from the GFL technique for the shaping of large SLS float glass was studied.

The reproducible preparation by levitation of ZBLAN (fluoride) discs of high optical quality was demonstrated in a one step procedure using NF_3 as reactive atmosphere on selected raw materials. Bulk scattering losses of 0.016 dB/km (extrapolated at the 2.55 µm wavelength) have been achieved along with concentrations of scattering defects as low as 25 per cm^3. These results means that a factor fifty improvement has been achieved compared to conventional routes and that the theoretical intrinsic limit is quite close.

Following those results with ZBLAN, the technological development of vertical levitators was engaged either for the molding of glass rods or for

the continuous synthesis of glass rods starting from powders. Difficulties were encountered with ZBLAN glasses and only small cylinders could be synthetised, 10 to 20 mm in height (Φ15 mm) or pre-cast **rods molded over** 10 mm in height (Φ15 mm). A major breakthrough was however demonstrated : liquid columns up to 15 cm in height (Φ 15 mm) have been successfully molded during orientations tests with water at room temperature. This last result confirms the real capacity of the technique to confine long liquid columns.

levitated S1S and ZBLAN glass discs have shown improved optical homogeneity properties compared to precursor glass and the levitation technique was found to be the only reproducible preparation route at this time to obtain ultra-homogeneous ZBLAN glasses.

New luminescence and refractive index data have been recorded for ZBLAN and float glass as a means of making quality control **for the levitation and float** processes. Tin profiles at the upper and lower surfaces of SIV glass products have been particularly characterised. For ZBLAN glasses, the tack of reference data has not allowed to obtain directly usable information.

Besides these achievements, a better and **more realistic view of the industrial interest of the** GFL technique has emerged and through the perfecting of the workprogramme, cross - fertilization between the S1S and ZBLAN activities has increasingly grown through characterisation activities and Gas Film levitation of glass discs. New ideas have emerged as the low cost planar waveguide and the dissemination of results through publications is in rapid progress. Finally, contacts established with university groups turned out to be positive. To day, several European groups are developing GFL activities directed towards material solidification and basic studies **in hydrodynamics.**

2. The consortium

2.1 Names and addresses of the partner organisations

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2.2 Consortium description

Alcatel Alsthom Recherche

Alcatel Alsthom Recherche (AAR) is the corporate research center of Alcatel Alsthom in France. It is working on the most advanced part of the research carried out in the Group and its research departments have close connections with the subsidiaries of Alcatel Alsthom. The research priority is to develop tools, techniques and materials needed by the subsidiaries in the following fields : telecommunications, energy and transports.
The role of Alcatel Alsthom Recherche in this project was : i) To coordinate the project, ii) To develop the Gas Film Levitation (GFL) technique, in close cooperation with CEA-CEREM, for the preparation of ZBLAN glass rods free of extrinsic light scattering centres and iii) To participate with the University of Clausthal and the University of Sussex in the basic studies on bulk and surface properties of ZBLAN glass.

Società Italiana Vetro

Società Italiana Vetro (SIV), Italy's largest glass industry is now a membre of the Pilkington Group. SIV is one important producer of float glass in Europe and one of the major producers of glass for the car and building industries. SIV has a strong experience in the preparation of raw materials, the fusion and the transforming of glass. The Research Department is involved **in fields** such as new chemical treatments of glasses, organic and inorganic coatings, physical and chemical characterisations, . . . SIV disposes of a laboratory (at San Salvo) aimed at assisting the production and working of glass.

The main role of **SIV** in this project was in the following actions : i) To prepare calibrated sodalime glass batches to be melted comparatively by CEA-CEREM using the GFL technique and by SIV using conventional routes, ii) To characterise sodalime starting materials and sodalime glasses in order to assess their bulk and surface properties (chemical, physical and mechanical} in cooperation with the University of Sussex.

CEA-CEREM

CEREM (Centre d'Etudes et de Recherches sur les Matériaux) federates, **works out and valorizes** CEA competencies **in the field of material** science and engineering. CEREM studies and develops new processes for the elaboration of metals, ceramics, glasses or organic materials in the form of bulk pieces, composites, single crystals or thin films as well as characterisation techniques for the determination of material properties or for process control. CEREM has initiated the research and development on the GFL technique and deposited the corresponding base patent. The GFL technique has been successful tested by CEREM on model liquids at room temperature and liquid metals, **oxides or fluorides** at high temperature either on ground or in microgravity parabolic flights.

The role of CEA-CEREM in this project was to promote the development of the GFL technique through the following actions : i) To prepare ZBLAN discs on a reliable basis having ultra low scattering losses approaching the theoretical limit of 0.02 dB/km at 2.55 µm, ii) To develop the vertical levitator technology (tubular membrane) in cooperation with AAR for the potential fabrication of ZBLAN glass preforms for optical fibres, iii) To apply the GFL technique to model and industrial sodalime glasses from precursor discs supplied by SIV. These reference samples (characterised by SIV and the University of Clausthal) have been assumed to give the intrinsic bulk and surface properties of sodalime glasses used in the car and building industries, iv) To evaluate others fields of applications of the GFL technique.

Technical University of Clausthal

The Group of Pr G.H.Frischat, at the Technical University of Clausthal (TUC), has a long time experience in glass science and microgravity experiments on-board sounding rockets and the Spacelab.

Its role in the project was twofold : i) To contribute in the basic aspects which relate to glass fining, homogenisation, heterogeneous nucleation of ZBLAN, solidification features of sodalime glass compositions, etc ii) To evaluate the relevance of GFL experiments in microgravity in the glass area.

Sussex University

The research group of Pr. Townsend has considerable experience in studies of defect properties in insulating materials. Its work has ranged from “fundamental” characterisation of defects in a wide range of crystalline and glass insulators, to “quality control” using luminescence and optical absorption including “applications” **where modifications** in the properties had been introduced by **ion beam irradiation.** The more recent applications include the first demonstrations of waveguide lasers and second harmonic generation formed by ion implantation in insulators and the introduction of new surface properties of glass after ion beam treatments.

Of relevance to the proposed work are the separation of surface and bulk composition changes using methods of cathodoluminescence, thermo-luminescence, optical absorption and refractive index data. Some of these techniques have been developed at Sussex by the construction of equipment which is not commercially available, i.e. thermoluminescence spectrometer of very high sensitivity.

3. Description of the achievements

3.1 Introduction

The objectives of this study were :

a) To experiment GFL on ZBLAN and sodalime silica glass compositions relevant for the optical fibre and the glass industries.

b) To find out or develop the most appropriate surface and bulk characterisation techniques for said glasses.

c) To supply new conclusive data on material quality improvements to be expected from GFL.

d) To further evaluate the possible applications of this technique.

3.2 Tasks organisation / objectives

The objectives were distributed in different tasks, namely dedicated to materials aspects, process aspects, basic studies and applications prospects. For clarity, the list of these tasks is given below along with the partners involved :

I. Material aspects/preparation (M)

M 1	Precursor material, oxide	SIV, TUC
M2	Precursor material, ZBLAN	AAR, CEREM

II. Process aspects (P)

P 1	Oxide discs	CEREM, SIV
P2	ZBLAN discs	CEREM
P 3	Horizontal levitation, ZBLAN rods	AAR
P4	Vertical levitation, ZBLAN rods	CEREM, AAR
P5	Gas flotation of large oxide plates	SIV, CEREM

III. Basic studies (B)

B 1	Control of glass fining & homogenisation	TUC, CEREM
B 2	Heterogeneous nucleation, ZBLAN	TUC
B3	Bulk optical properties, ZBLAN	AAR, Sussex
B 4	Surface properties, ZBLAN	Sussex
B5	Bulk properties, oxide	SIV, Sussex
56	Surface properties, oxide	SIV, Sussex

IV* Applications prospects of the GFL technique (A)

A1	Fields of applications	CEREM, TUC

3.3 Main results

The main outputs of this project will be summarised in three parts, namely :

i) Fluoride glass results (Tasks M2, P2, P3, P4, B1, B2, B3 and B4).
ii) Oxide glass results (Tasks MI, PI, P5, B1, B5 and B6).
iii) Applications prospects of the technique (Task A1).

3.3.1 ZBLAN Glasses

1. Preparation of ZBLAN glass discs

a) Experimental work

The GFL process had to be optimised for the preparation of ZBLAN glass discs, typically 20 mm in diameter, having ultra-low losses using a specific Test Levitator equipment installed at CEREM. A general view of the system is shown in figure 1. The Levitator vessel with the high temperature components are represented in figure 2.

Operating conditions such as membrane properties, powder conditioning by in-situ reactive processing, composition of the levitation and ambiant gas, fining and cooling programme had to be varied and properly adjusted. Following the selection of suitable powder raw materials (from Merck, Morita and Cerac companies) and a detailed study of each stage of the elaboration process, a single step process of successful elaboration was defined. Reactive Atmosphere Processing (RAP) of the levitated molten glass by SF_6 or by SF_6+NF_3 gases in alternance were studied.

A large number of high quality ZBLAN glass discs (figure 3) have **been** prepared by containerless RAP of the elementary fluoride powder mixtures by Gas Film Levitation (see table 1). Glass compositions were 53 ZrF_4, 19 BaF_2, 4 LaF_3, 4 AlF_3, 20 NaF and 54 ZrF_4, 23 BaF_2, 4 LaF_3, 3 AlF_3, 16 NaF {mole%). Glass samples characteristics were : Mass: # 6 g, diameter : # 20 **mm, thickness:** # 6 mm.

All these samples were characterized for glass density, concentration of light scattering defects by Laser Scanning Tomography (performed at the Montpelier University] and scattering losses at five wavelengths (0.488 to 1.3 µm) using the optical bench developed at AAR (table 1}.

Among these samples, 8 were selected and shared between other partners for complementary characterisation by various techniques:

- Luminescence, University of Sussex
- Homogeneity of the refractive index, University of Clausthal
- Differential Thermal Analysis, refractive index and critical cooling rate, (University of Rennes).

b) Analysis of Results

Reactive processing using SF_6 and NF_3 (in alternance) has definitely proved to be superior to processing with SF_6 only especially regarding the reproducible preparation (66%) of high optical quality glass discs. The introduction of RAP by NF_3 has shown to be very efficient in reducing the concentration of light scattering centres to values reliably below 500 cm^{-3}, with the lowest observed values below 50 cm^{-3} (see table 1). In addition, all the samples **processed under** NF_3 exhibited a pure Rayleigh behaviour (variation of scattering losses vs wavelength according to a λ^{-4} law) **between** 0.488 and 1.3 µm (figure 4). According to Mie's theory of light scattering by spherical particles, this behaviour should be also observed up to the range of fluoride glasses ultra-transparency near 2.5 pm. From the detailed analysis of the spectral dependence of the scattering losses, it was found that the remaining defects could correspond to ZrO_2 particles with average diameter below 0.2 pm. At this level, these particles will follow a Rayleigh law in the infrared wavelength range and their contribution to the **overall** scattering losses will be negligeable.

II. Levitation of ZBLAN glass rods

a) Horizontal levitation

The basic boat-like horizontal levitator has been modified in order to overcome the impossibility to prepare rods with the circular cross-section basically required for optical fibre preforms. The new configuration used a membrane with a quasi-circular cross-section and two diffusing pistons aimed at the lateral positioning of the glass drop and expectedly at the compression of the molten drop. Numerous experiments were conducted with this equipment using either precursor pressed powder rods, precursor glass **rods (about 50 experiments} or test liquids simulating the properties of molten glass at different processing temperatures.** On the basis of this experience, a procedure was found **whereby quasi-circular glass rods could be prepared from pressed powder rods.** This procedure involved the

preparation of pressed powder rods of relatively small diameter as compared to the membrane, the melting of the rods and the compression of the molten drop by the displacement of the opposite pistons. Experiments have shown that end piston wetting and parameters adjustments could be critical with this horizontal structure especially with low viscosity liquids.
Said structure has therefore been abandoned for the vertical system in the case of ZBLAN glass. It may prove effective in the future for other compositions.

b) Vertical levitation

Basic equipment for glass molding

A new basic equipment for the vertical tubular levitation has been designed by CEREM in order to study the contactless molding and continuous casting of small diameter rods (Φ 15mm, Length 50 mm). Basic studies (thermal instabilities, hydrodynamic instabilities, water molding tests and molding of glass rods) relevant of this new process have been carried out in order to prepare a ZBLAN rod with a precursor rod made by AAR.

The equipment has a casting device in which the rod is levitated and molded. Directional solidification can be achieved by three ways : i) guided translation of the furnace {gradient deplacement}, ii) guided translation of the sample (sample throughput) and iii) decrease of the furnace temperature (thermal gradient decrease). Figure 5 presents a general view of the facility.

The design of this new facility was based on :

requirements for a creative and efficient, low cost, fast, realistic, flexible multi-step and iterative development plan,
analysis of the physico-chemical and thermal requirements for preparation of high quality fluoride glasses,
dimensional and stability requirements for the low viscosity, contactless molded glass melt.

Water molding tests have been worked out. Water enables a room temperature validation in a pessimistic configuration compared to most materials due to its low viscosity. Liquid mass oscillations are characteristic of the sample physical properties. The appearance threshold of these oscillations is an increasing function of the viscosity, the damping time is a decreasing function of it. The weaker is the viscosity, the sooner appear the

liquid mass instabilities. The oscillation frequency is correlated with surface tension.
Given a good set of parameters (differential pressure drop across the membrane, injection technique), water columns up to 150 mm in height have been successfully molded.

First trials have **been carried out with** glass rods. Firstly with AR Schott glass (Sodalime silica) for orientations tests as this type of glass is less sensitive to crystallisation than ZBLAN fluoride glass. AR glass **rods have been** successfully molded under argon atmosphere over 30 mm at temperatures above the vitreous transition temperature (720 to 920°C). Secondly, starting from calibrated ZBLAN glass rods (Φ 15 mm, Length 50 to 70 mm), two molding experiments have been made under argon atmosphere at 320 and 350°C (60 and 900C above the vitreous transition temperature). [n this case, molding was effective over 15 mm in height but **surface devitrification was observed** in the molded parts. Figure 6 shows molded AR and ZBLAN glass rods. SF_6 was not used in the levitation gas, which can explain the partial surface devitrification of ZBLAN due to slight residual water corrosion. Further work still **needs** to be done to master the parameters in the case of ZBLAN glass rods to improve the temperature/atmosphere /devitrification /deformation conditions.

Continuous fabrication of glass rods

AAR had to optimise its prototype vertical levitator equipment to demonstrate the feasibility of the process. This prototype had to be completed to eliminate dust and water contamination in sensible areas. Specific operating conditions had to be determined for the replenishment of the molten ZBLAN drop (Φ 15 mm, 5 to 10 mm in height) by powders to achieve a continuous fabrication of ZBLAN glass rods (up to 50 mm in length).

The vertical levitator facility installed at AAR may be described by its different functional elements :
- The levitator itself integrated in a silica liner
- The pressure control **(sensor, regulator, mass flow meter)**
- The motorized injection and translation system
- The powder replenishment system
- The heating system (HF generator, coil, regulator)
- The fluids control box
- The gaz extraction

- The laminar flux bench

Figure 7 shows a picture of this levitation facility.

The main actions dedicated to the development of the vertical levitator for the preparation of fluoride glasses were centered on the optimisation of different functional parts of the system. Major modifications had to be made to solve encountered problems and a special attention had to be devoted to the reliability of the process through a better control of the tolerances (1 O µm adjustments) of graphite pieces constituting the levitator (membrane, pedestal, piston).

Theoretical numerical simulations (thermal transfers, fluid mechanics) have been initiated to possess a better understanding of the process. Experimental tests at room temperature were carried out to further characterise the levitators, especially regarding the liquid column stability versus supply pressure.

Numerous experimental runs (about 90) were done with ZBLAN glass melts taking into account the accumulated knowledge given by the parallel actions. Specific behaviour due to the characteristics of the glass melt itself (low viscosity, large density, moderate surface tension] was noted upon heating at fining temperatures. To increase the height of confined melt, a powder replenishment system was continuously improved to approach better conditions. This last step, i.e. the powder replenishment of the melt to fabricate large rods, was not fully overcome. The main difficulty was to perform a stable powder flow rate over 15 minutes without wetting of the glass melt on the porous membrane wall. Figure 8 shows a typical ZBLAN glass cylinder recovered after levitation on its graphite pedestal (Φ 15 mm, 12 mm in height).

Vertical levitation was shown to be an efficient technique to confine long and perfectly circular liquid columns (i.e. over 150 mm with water). Several details have to be resolved to achieve large glass rods and especially regarding the filling control to increase the height of the final cylinder.

III. Characterisation of ZBLAN glasses

The outstanding results obtained in term of light scattering have already been mentioned in § 3.3.1, part I.b.

III. 1 Glass homogeneity

The optical homogeneity of levitated and crucible-made ZBLAN glasses was quantified according to the Christianson-Sheiyubskii method (Refractive index variations, see figure 9). Qualitative information was obtained by Scanning Electron Microscope (SEM) observations. The main results converge towards the conclusion of an improved homogeneity through GFL processing.

III.2 Glass heterogeneous nucleation

The critical cooling rate and sensitivity of ZBLAN glasses regarding heterogeneous nucleation and crystallisation have been studied by the well known TTT (Time-Temperature-Transformation) method. The experiments have been carried out on crucible-made glasses and not on levitated glasses. Following results **have been obtained :**

- The nucleation rates previously determinedby Drehman (Mat. Sci. Forum, 19-20 (1 987) pp. 483) were confirmed (4, 105 cm^{-3}see-' at 265°C)
- The crystal growth rate determined by SEM is lower by two orders of magnitude than the one obtained by optical microscopy (0.6 µm/min at 350°C)
- Correspondingly, the critical cooling rate (heterogeneous nucleation) has a high value of 236 K/rein compared to literature, which however can be confirmed by models for the assumed residual crystalline volume fraction of 10-6.
- This critical cooling rate can be increased by a factor of four, if nucleating agents are added ($AgF, PtCl_2$). Whereas the crystal growth parameters remain unchanged, this increase is caused by an enhanced nucleation rate (two orders of magnitude higher].
- Nucleating agents act as catalysts; accelerating crystallisation processes without an influence on the crystallisation mechanism (shape and composition) as demonstrated by examinations using SEM, AFM and XRD.

III.3 Luminescence measurements

a) Bulk optical properties of ZBLAN

Radioluminescence (RL) and thermoluminescence (TL) spectra have **been recorded from a number** of ZBLAN samples, including levitated and crucible processed material (typical RL emissions about 340, 370 and 420 nm, RL exampie in figure 1 0a).

The differences in the spectra related to the method of sample preparation are consistent with the presence of fewer intrinsic defects and impurities in the levitated glass. Whilst this is not unexpected, luminescence from these systems has not been extensively studied elsewhere, and the ability to compare the two types of material resulted in the suggestion that luminescence could be used as a quality control for the glass production.

Thermoluminescence above room temperature was also measured in ZBLAN for the first time (example in figure 10h]. The data reveal that after relatively small X-ray irradiation doses the glass is less thermally stable than the unirradiated material and results in bubble formation and decomposition at relatively low temperatures during the TL measurements. Such decomposition at these dose levels was not expected and further studies of the radiation stability of the glass may be needed. In normal usage of fibres it is unlikely that material would be deliberately irradiated and then heated, but the data suggest some caution and further tests would be required if this possibility exists.

Parallel measurements with other fluorides has enabled progress to be made in recognizing the similarities in the TL behaviour of ZBLAN and other fluorides. In data with some fibre samples the presence of rare earth dopants was clearly apparent.

b) Surface studies of ZBLAN

To separate surface and bulk properties, the luminescence signals of surfaces were recorded with cathodolumi nascence. Significant differences were apparent between crucible and levitated glass (figures 11a and b}, and some differences were apparent between upper and lower sample faces. This points to reactions with the crucible walls (most probably the Pt) and also shows that the circulating pattern in the melt does not give a uniform distribution of imperfections for the small samples.

3.3.2 SLS oxide Glasses

I. Classical preparation of S1S glasses

Several SLS glass samples have been prepared in order to be levitated using the CEREM Test levitator and for characterisation purposes. The following set of samples have been produced:

- Precursor sodalime samples, disc-shaped, in various diameters and thicknesses;
- Glass samples electrically melted in platinum or alumina crucibles;
- Segment of sphere-shaped samples taken from the doghouse zone of the Float line,
- Glass powder of suitable granulometry.

Samples of raw materials and/or glass were sent to the various partners for basic studies.

II. Levitation of SLS glass discs

Two dedicated Levitator facilities were used to levitate a large number of SLS glasses starting from precursor samples from different origins (Schott AR glass, Float glass discs, Crucible-made glasses, Dog-house samples). A first levitator allows levitation up to 1700°C under neutral atmosphere on graphite diffusing elements (figure 12). A second levitator works under air atmosphere up to 1600°C with oxide ceramics diffusing membranes.

A large number of samples (about 100) were levitated under different conditions (temperature, time, atmosphere] giving mostly levitated discs 10 to 15 g in weight and about 30 mm in diameter but successful trials were achieved with glass lenses up to 50 g in weight and over 50 mm in diameter {see table 2).

SLS glasses processed under inert atmospheres (argon and nitrogen) with graphite diffusing elements presented poor optical properties. Bubbles coming from surface roughness, scratches or splinters of the precursor samples were observed for processing temperatures below 1000°C. Brown-reddish coloration and strong refractive index variations were present when the glasses were processed at higher temperatures.

Compared to the reference crucible precursor samples, samples GFL processed at 1300°C-3hours in air were significantly improved although still of poor homogeneity. Similar precursor samples GFL processed at 1450°C-

3hours in air showed significantly higher homogeneity but still present residual striae observed by the naked eyes.

At this stage of the study, specific procedures should be refined to improve the sample homogeneity through preparation of finer raw material powders, higher GFL fining temperature and longer fining time.

III. Levitation of large **SLS** glass pieces

III.1 Processing of large glass **discs**

An upgraded version of the high temperature levitator was used in this case with graphite diffusing elements. High quality SLS (float glass), borosilicate (Pyrex) glass discs and cylindrical precursor samples were used as starting materials.

Precursor samples were shaped by machining or by in situ softening in contact with the graphite diffusing element at moderate temperature (800 and 900°C for SLS and Pyrex glasses respectively).

Successful contactless processing of SLS glasses have been achieved with sample masses up to 160 g and sample diameter approaching 80 mm at higher temperatures (1 000 and 1250°C **for** SLS **and** Pyrex glasses respectively). Contactless processing of a SLS sample with mass approaching 200 g was interrupted by overflow of the molten glass outside the diffusing element. Figure 13 shows the precursor and GFL treated sample shapes.

These new results demonstrated the ability for GFL to levitate masses 10 times as usual by gas fim levitation and a **one thousand time higher sample volume and mass than** any other containerless processing technique for glasses.

III.2 Shaping of float glass plates

During the course of the project the initial objective (production of large area glass plates by GFL) proved to be not feasible for SIV. The proper GFL process is still a laboratory technique, not yet mature for the extension to large scale processes. **An alternative** process, the “flotation process”, in some way linked to the proper levitation process was studied in order to produce large oxide glass plates.

This "flotation process" **consists of a refractory case** where molten glass can be formed and successively levitated (floated) on a floating bed. The suspension medium is air, properly heated in a heat exchanger. The following benefits can be expected by this process:

the bottom surface undergoes a sort of "fire polishing" and, as a consequence, a reduction of the surface rough nesses, which are responsible of the optical quality;

- the planarity of the system is assured if air distribution is accurate;
- limited contact of the glass with extraneous materials related to an improvement of the glass mechanical properties.

Low temperature trials have been carried out in order to establish the flow rate and the consequent pressure field at the floating, bed. By this process some 20x30 cm^2 have been produced; their quality must be improved but the results are encouraging. A picture of the laboratory plant is shown in figure 14.

IV. Characterisation of S1S glasses

Glass homogeneity and chemical composition changes of SLS glasses have been investigated as a consequence of their production process and subsequent levitation (as far as possible).

Three types of industrial samples and one crucible glass have been taken into consideration:

- Doghouse Samples : that is glass at the first stage of melting;
- Refining Samples : that is well homogenised glass before the forming process;
- Float Glass Samples : taken from the end of the line
- Model Sodalime Glass Sample : ultra-pure raw materials melted in a sillimanite crucible.

IV. 1 Homogeneity (refractive index variations)

The application of the Christiansen-Shelyubskii technique has confirmed the obvious inhomogeneity of the glass at the "Dog-house" stage (figure 15a).

The bests results are obtained for the "refining and "float line "glasses (figure 15a), with an increase **in homogeneity as the permanence time into the furnace increases; this improved homogeneity, in comparison with that one of the crucible** glass sample, is **due** to the higher glass volume/refractories surface ratio which can be observed in the industrial process.

Small size crucible glasses exhibit bad homogeneity properties whereas good results are obtained with levitation (90% max. transmission , figure 15b).

IV.2 surface characterisation

a) Chemical analyses

Extensive analyses of the surfaces of the float and crucible-made glasses were carried out using luminescence, optical waveguiding (for refractive index measurements), secondary neutral mass spectroscopy (SNMS) and ion beam techniques which have been applied for the first time to our knowledge to the entire width of a float line (2.8 meters).

Specially interesting results have been obtained regarding the concentration profiles of Fe, Na, S and Sn across the glass and along the various stages. The redox chemistry of tin at the surface of floated glass appears to still **need some clarification.**

b) Mechanical properties

The improvement of mechanical strength of SLS float glass was one of the important objectives of the project for the car window application. During the course of the project, the preparation of large glass plates (Task P5) was re-oriented with the preparation of large oxide discs by CEA-CEREM (§III. 1) and the study of a flotation process for shaping of glass plates by SIV (§III.2). As a consequence, no levitated glass plates were available to perform the mechanical tests as classically made on large float glass pieces. Mechanical tests on large levitated oxide discs were not feasible with the equipment available at SIV; the curved surface of a levitated disc make this test particularly difficult. On the other hand, pure mechanical tests to compare the strength of a GFL glass disc and a Float glass plate have little significance. More meaningful would be to test the surface of levitated samples using adapted tools and techniques such as indentation methods, rugosity measurements or adhesive tests but these experiments were not viable by the required time.

Hardness and bending tests have been done on industrial float glasses with various treatments and the results have been compared for different types of glasses. **These results make** up the basis of the future comparison with levitated glass samples.

3.3.3 Applications prospects of the GFL technique

Potential applications of the GFL technique have been reviewed for earth-bound applications as well as for space-bound applications. For earth-bound applications, the main fields seems to be the following ones :

a) Basic science study of the liquid state (in-situ characterisation, undercooled state properties, nucleation mecanisms, thermo-physical properties).

b) Preparation of material samples for further solid-state characterisation (glassy materials, crystal growth from the melt or from solutions such as proteins].

c) Preparation of mid-scale reference material samples or intermediate state industrial “half-product” (precursor rod for further fibre drawing, laser rods or wafers, substrate materials for further epitaxy or integrated optics components).

d) Manufacture of ready-to-use industrial product (for improved optical, mechanical or chemical properties such as lenses, viewports, weathering resistance, good surface state for further surface treatment).

Concerning space-bound applications, the combination of containerless processing and microgravity conditions offers outstanding opportunities for either in-situ studies of the basic physics of solidification or synthesis of reference material samples for further ground level characterisations.

Microgravity conditions (10-2 to 10^{-6} g) provide the same reduction ratio for gravity and buoyancy forces, sedimentation, buoyancy convection and hydrostatic pressures. In this way the relative importance of other parameters is increased, and there are favorable conditions for studies of non-gravity driven phenomena of importance in materials processing such as : convective flows (e.g. induced by surface stresses], transport phenomena (diffusion, capillary effects) or weak interactions (evolution of dispersed phases).

Different gas film levitators for containerless processing of materials in microgravity conditions have been developed by CEREM under ESA and CNES fundings. Positive tests in microgravity conditions (containerless positioning of large water samples) in "CARAVELLE ZERO G“ parabolic flights have been made using a fully automated, reprogrammable test bench (figures 16a and b).

In the field of glass **science,** the **Technical University** of Clausthal participated to space experiments (not with GFL) on-board sounding rockets or in the Spacelab. Different intrinsic data are provided, describing pure atomic or molecular effects with the following subjects : shrinkage of gas bubbles **in melts,** interdiffusion/self-diffusion between melts, homogeneity of glasses, irradiation of glasses, corrosion, production of new compositions, production of new glass-metal and glass-ceramic-metal composites.

4. Exploitation **plan**

Besides the very significant progress achieved in **term of scientific or** technical knowledge, two main results can be outlined

- the reproducible preparation of special glasses (ZBLAN) with high optical quality (bulk and surface),

- the improvement by an order of magnitude of the capacity of the technique **for classical** oxide glass discs.

[t appears **however that** GFL is not **mature** for direct implementation in any of the field which had been previously considered that is optical fibres and float glass industry.

CEA-CEREM is the only identified organisation to develop aerostatic levitation processing technique and has the intention to further develop at this time the Gas Film Levitation technique following the useful results obtained within the frame of this contract.

The main advantages of the GFL technique compared to competitors (other levitation techniques) are the following ones :
- Large volume or weight of the levitated samples (>100g).
- independence between the levitation process and a reliable temperature control (the levitation process doesn't heat the sample),
- Levitation of all types of materials,
- Direct shaping during fabrication,
- Use of inert or reactive gas as required by purification or fining purpose,...

Various industrial applications have been identified by CEA-CEREM according to the performances or advantages of GFL process and products :

- Processing of ultra-transparent glass (without scattering defects)
  * Special glasses [disk or rod for optical systems]
  * Components for optical systems i.e. 2-4 µm 1. R. sensors
  * Waveguide substrate for optoelectronics devices

- Processing of "as-molded surface" glass (no surface contamination}
  * Waveguide substrate (see before)
  * Lenses or shaped optical components with high surface quality (Optical, photographic equipments)

- processing of controlled chemical composition glasses
  * Reference samples
  * Specific composition samples (non achievable by conventional route) : Laser glass, waste management [irradiated materials storage glass)

- Processing or treatment of non-glassy or vitreous materials
  * Processing of superconductors, ceramics, proteins crystals
  * Purification of materials

- Physical characterisation tool (scientific experiments)
  * Undercooked liquid state studies

5. Collaboration sought

The GFL process has been patented by CEA-CEREM for a broad variety of applications in the field of material processing by the patent no FR 2.509.637 (EN 81. 13966); "Procédé de traitement de masses liquides saris contact avec [es parois d'un dispositif et application à la mise en forme de matériaux en microgravité".
Specific applications in glass processing have also been patented by Alcatel Alsthom Recherche, no EN 89.09123; " Procédé de fabrication en continu d'un barreau de verre, notemment pour la réalisation de matrices laser ou de préformes pour tirage de fibres optiques" and no EN 92.00867; "Procédé de fabrication d'un tube en verre, notamment en verre fluoré".
The vertical levitator process and facility has been patented by CEA during this contract ; "Procédé et installation de sustentation d'une masse liquide par un film de gaz ".

CEA-CEREM is currently looking for industrial partners to transfer or to develop the GFL technology on new applications. For that purpose, specific actions will be engaged, i.e. :

- To protect industrial property by patents on process, systems and applications,
- To promote the results in the scientific field by publications, conference participation (several papers are planned in 1996 by the different partners) and by the development of contacts with universities or research laboratories,
- To promote the ultimate and reproducible performances on ZBLAN samples in the business field : business magazines, exhibitions, industrial fairs,...
- To contact EEC through the "Value" program,
- To perform a value analysis of the process,
- To engage few preliminary industrial contacts,
- To schedule a market study (cost : 30 to 50 KECU).

In addition, CEA-CEREM participates to scientific containerless program (scientific cooperation through the CEA-Grenoble Drop Tube). Contacts have already been engaged by the Max Planck Institute of Stuttgart for a cooperation ; the objective is to study liquid state properties of undercooked materials by the gas film levitation. It is scheduled to ask for an European support {human mobility} for this cooperation.

6. References

6.1 Publications resulting from the project

Can, N., Kazanci,N.,Townsend,P.D. and Chadwick, A. V., "Cathodoluminescence emission spectra of Nd doped CaF2", Phys Stat Sol (a) 146, 843-852, 1994.

Yang, B., Townsend,P. D. and Holgate,S.A.,"Cathodoluminescence and depth profiles of tin in float glass.", J Phys D, 27, 1757-1762, 1994.

P. Baniel, O. Blanc, S. Lempereur et J. Granier, "Caractérisation optique de verres fluorés élaborés en levitation sur film de gaz", Proceedings" 15th JNOG 95, Nov. 6-8, 1995, Palaiseau [France}.

A. Janke and G.H. Frischat, "Determination of the critical cooling rate of heavy metal fluoride glasses (ZBLAN) containing nucleating agents",

presented at the 10th International Symposium on Non-Oxide Glasses, June 19-22, 1996 in Corning, N. Y., USA., to be published in the Journal of Non-Crystalline Solids.

Yang, B. and Townsend, P. D., "Cathodoluminescence of NaF", Phys Stat Sol (b), 182, K39-41 , 1994.

Townsend, P.D. and White, R., "Interpretation of rare earth thermoluminescence spectra", Rad. Protect. Dosim, in press.

In preparation or submitted :

F Lamouroux, et al, "Ion beam analysis of float glass surface composition", J. Non-Cryst Solids ?

B Yang and P D Townsend, "Thermoluminescence of rare earth doped LaF_3" Phys Rev B?

S A Holgate, A-K Jazmati and P D Townsend, "Thermoluminescence spectra of alkaline earth fluorides", Phys Stat Sol (b) ?

P D Townsend, B Yang, "Thermoluminescence and cathodoluminescence of ZBLAN", J Phys D?

P D Townsend, "Direct **transitions between trap and recombination centres** during TL", Rad. **Meas.**

6.2 Other publications

Related publications stimulated in part by this project :

Khanlary,M-R., Townsend,P. D. and Townsend,J. E., "Radioluminescence response of germanosilicate optical fibres", Radiation Effects, 127, 47-59, 1993.

Khanlary,M. R., Townsend,P. D. and Townsend,J. E., "Luminescence spectra of germanosilicate optical fibres I - Radio- and cathodoluminescence", J Phys D 26, 371-378, 1993.

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Holgate, S A, Sloane, T H, Townsend, P D, White D R and Chadwick A V, "Thermoluminescence of calcium fluoride **doped** with neodymium", J Phys Condensed Mater, 6, 9255-9266, 1994.

Rendell, H. M., Luff, B.J. and Townsend,''Thermal treatments and emission spectra of TL from quartz", Rad Measur, 23, 441-449, 1994.

McKeever, S. W. S., Moscovitch, M and Towns end, P. D., "Thermoluminescence dosimetry materials: properties and uses", Nuclear Technology Publishing, Ashford, 1995

P. Baniel, A. Lopez, P. Gall, J. Granier, "influence of processing parameters on the scattering properties of fluorozirconate glasses prepared by the gas film levitation technique", presented at the 13th University Conference on Glass Science, August 9-11, 1995, RPI (Troy, NY), to be published in 1996 in the Journal of Non-Cryst. Solids.

External Publications :

K. Högerl, G.F. West, Homogeneity of fluoride glasses, Glass Technol. 36/4 (1 995) pp.1 35-138.

TABLES AND FIGURES

Table 1 : Results of Laser Scanning Tomography (defects concentration) and bulk light scattering measurements of levitated ZBLAN glasses.

	Powder features			Fining Steps Parameters						Laser Tomo-graphy	Bulk scattering losses vs wavelength (approximated Mie equatior coefficient: s)		
1 Sample N“	2 % NaF	3 Origin	4 Supplier	5 Gas	6 Temp. (°C)	7 Duration (minutes)	8 Gas	9 Temp. ″C	10 Duration (minutes)	11 Defects Conc. (cm^{-3})	12 c	13 b	14 a
08-075	16	AAR	MoMCCM				SF_6	750	25	938	/	0.029	0.767
-076	-								-	8390	/	0.187	0.745
-078	-								35	2580	/	0.224	0.743
-073	-								-	4048	/	0.158	0.767
-052	-								45	1418	0.002	0.050	0.757
-053	-								-	5020	/	0.079	0.849
-088	-								-	2950	/	0.165	0.776
-087	-								60	681	/	0.009	0.767
OB-082	-	CEA	BMCCM						30	2160	/	0.097	0.782
-081	-								45	2110	/	/	0.807
-102									-	1600	/	/	0.779
-105									-	97	/	/	0.752
-107									-	5437		0.206	0.717
08-084				SF_6	750	45	NF_3	560	30	44	/	/	0.809
-098								570	30	103	/	/	0.784
-103										319	/	/	0.780
.109										454	/	/	0.788
-104									-	25	/	/	0.772
-085								620	30	110	/	/	0.804
-090									-	368	/	/	0.790
m		AA R	MoMRRM				SF_6	750	45	18300	/	2.55	0.480
		CEA	BMBBB						-	426	/	/	0.876
									-		0.002	/	0.900
			BMCCM				-	-	-	1298	/	0.018	0.883

Legend of the columns :

1 Sample reference. 2 Variation on sample composition. 3 Origin of powder blends. 4 Supplier code: C: Cerac, B: BDH, M: Merk, Mo: Morita, R: RMC.

5-10 Successive treatment with SF6, then NF_3-containing Argon atmosphere. 8-10 **Treatment with only** SF_6-containing Argon atmosphere.

11 Concentration of scattering defects. **12-14** Coefficients of the approximated Mie equation for the total scattering losses : $\alpha_{sc.}=a/\lambda^4+b/\lambda^2+c$

Table 2 : GFL Processing of Float glass disc precursor samples from SIV at CEA-CEREM.

Sample Number	Precursor Dimensions D (mm) x H (mm)	Diffusing **Assembly** Mat. **(Dim.)-N°**	High Temp. GFL Processing		GFL Processed Sample		
			T ("C) - Time - Atm.	Mass loss **(mg)**	Mass (9)	Diameter (mm)	Height (mm)
FGD-1	D30 H8	G(R50D39/45)	10400C - 1hr - Ar	1.0	13.36	31.52	9.69
FGD-2	D30 H8		1120°C - 1 hr - Ar	2.6	13.19	31.34	9.53
FGD-3	D30 H8		1200 C-15 min - Ar	2.1	13.33	31.47	9.67
FGD-4	D30H12		1200"C -1 hr - Ar	7.6	20.49	37.33	10.62
FGD-5	D30 H12		1040°C - 1 hr - Ar + turned up-down 104OOC.1 hr - Ar	1.3 1.1	20.43 20.43	37.28 37.28	10.63 10.63
FGD-6	D30 H12		1200°C -5 min - Ar polished on top, turned up-down 120@c - 5 min - N_2	1.7 1,0	20.40 19.69 19.69	37.24 36.75	10.61 9.75 10.53
FGD-7	D30 H12		104OOC-1 hr - N_2	1,8	20.48	37.28	10.66
FGD-8	2x D3OH1O	G(R50D69/75)	1OOOOC-1 hr-N_2	2.5	33.68	45.04	12.34
FGD-9	D3OH1O	"	850°C -1 hr - N_2	0.3	16.75	34.93	9.85
FGD-1O	2x D30 H15	G(R50D69/75) "	1000°C - 2 hrs - N_2 + 1040°C - 10 hrs - N_2	n.m	n.m 53.27	n.m 53.00	n.m 14.50
FGD-11	D30 H8 + D30 H4		1200°C - 1 hr - N_2	9.5		36.69	10.51
FGD-12	D30 H8 + D30 H4		1300°C - 5 min - N_2				
FGD-13	2 x D30 H6		1300°C -90 min - N_2	27.1	19.85	36.81	10.59
FGD-14	2 x D30 H6		1400°C - 15 min - N_2	34.6	19.8	36.78	10.58
FGD-15	D30 H6 + D25 H8		1400°C - 2 hrs - N_2	217.0	19.22	36.38	10.50
FGD-16	D30 H4 + D25 H12		1400°C -3 min - N_2	18.3	21.12	37.71	10.74
FGD-17	D30 H4 + D25 H12		1400°C - 15 min - N_2	41,1	20.92	37.60	10.71
FGD-18	D3OH1O+D25H1O		14000C -15 min - Ar	**20.5**	**11.87**	30.00	9.47
FGD-18'		SA(R50D39/60)-5	1300°C -2 hrs - AIR	15.1	11,87	30.10	9.36
FGD-18"		"	13000C -12 hrs - AIR	19.2	11.85	30.1	9.32
FGD-19	D25 H8		1400°C -15 min -Ar	14.9	9.50	27.39	9.02
FDG19'		SA(R50D39/60)-1O	1350°C -2 hrs - AIR	(*)	(*)	(*)	(*)
FDG20	D25 H8		1400°C - 15 min - Ar	15.9	9.49	27.38	8,99

(*) Sample and diffusing assembly destroyed by wetting.

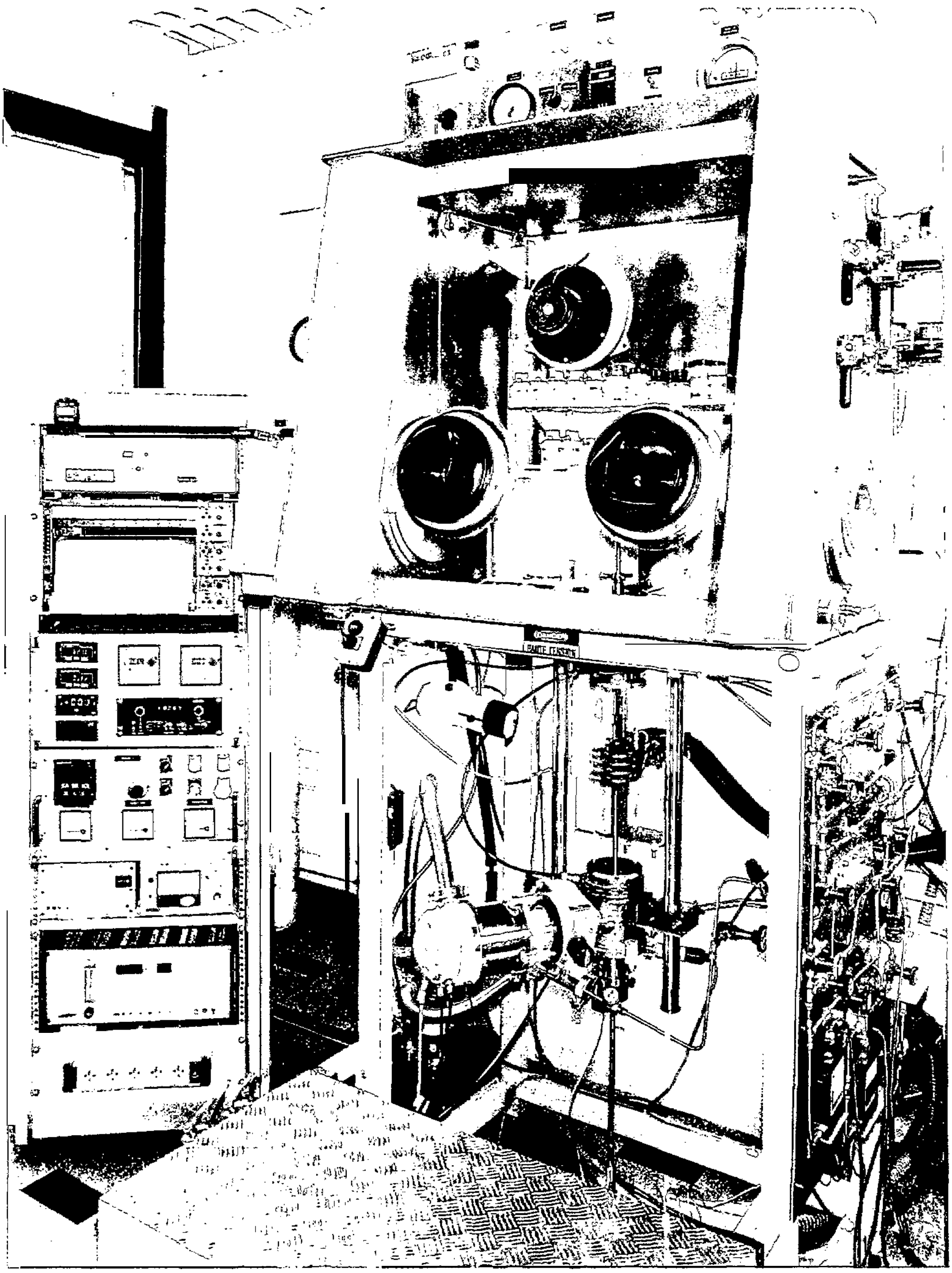


Figure 1 : Test Levitator - Overall view of the facility.

1 - Solid or Liquid sample.

2 - Graphite diffuser.

3- Graphite susceptor.

4- HF induction coil.

5- Thermocouple (type K).

6- Thermocouple (type K).

7- Levitation gas input.

8 - Levitator vessel flushing gas input.

9- Levitator vessel gas output.

10 -To Vacuum pumps.

11, 12- Diffuser support water cooling circuit.

13, 14- Levitator vessel water cooling loops.

15- Glove box floor.

16- Connecting flange between glove box and Levitator.

17- Vitreous Silica tube.

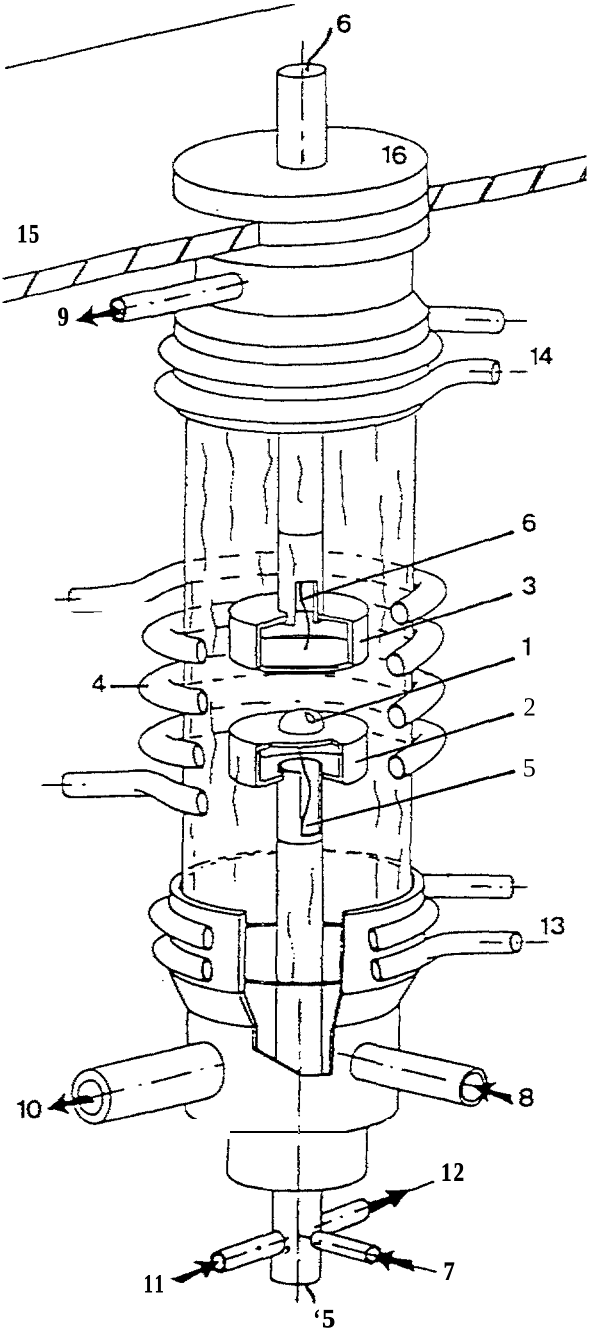


Figure 2 : Test Levitator - Detail of the levitator vessel.

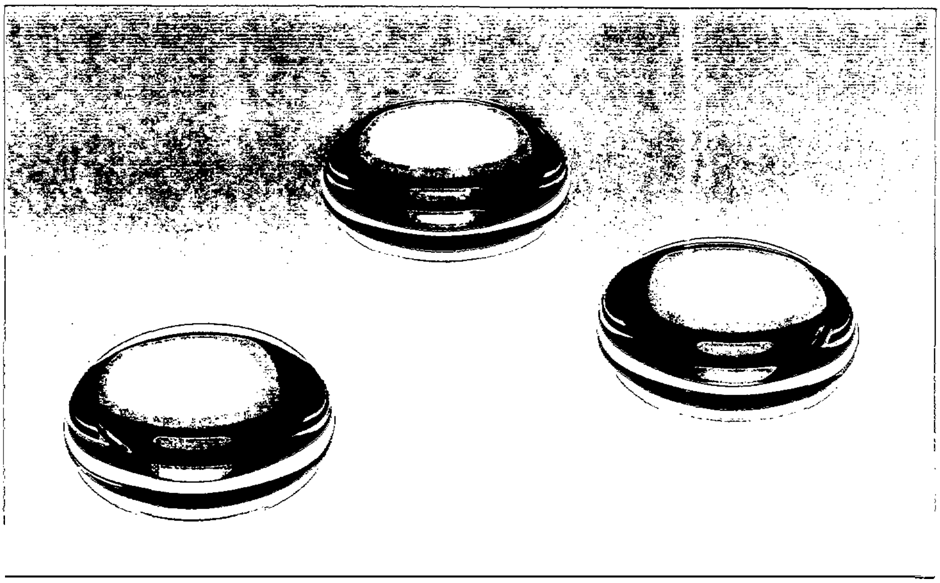


Figure 3 a) : Typical ZBLAN glass discs prepared by GFL (ϕ # 20 mm).

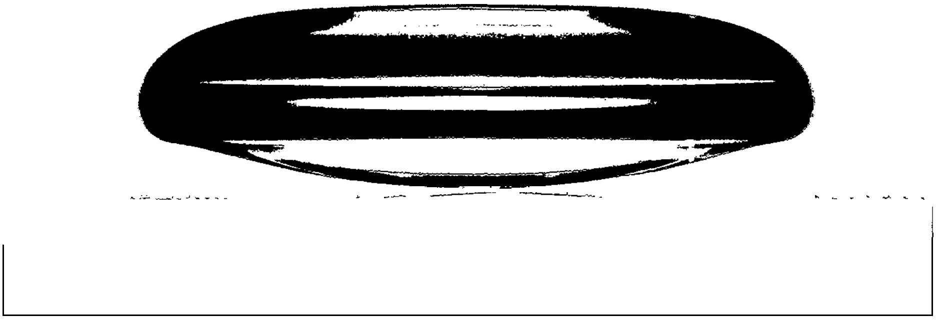


Figure 3 b) : Profile of a levitated ZBLAN glass disc.

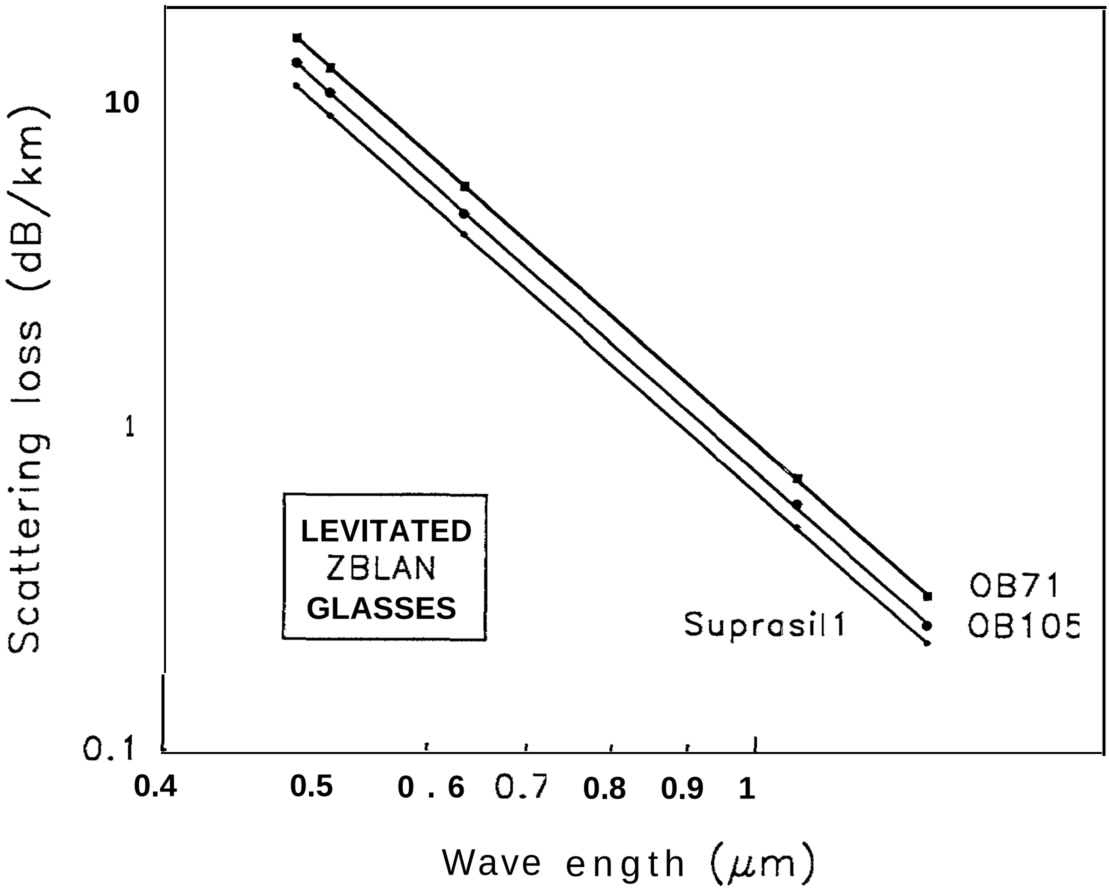


Figure 4 : Scattering losses versus wavelength of levitated ZBLAN glass discs as compared to those of Suprasil 1 reference sample.

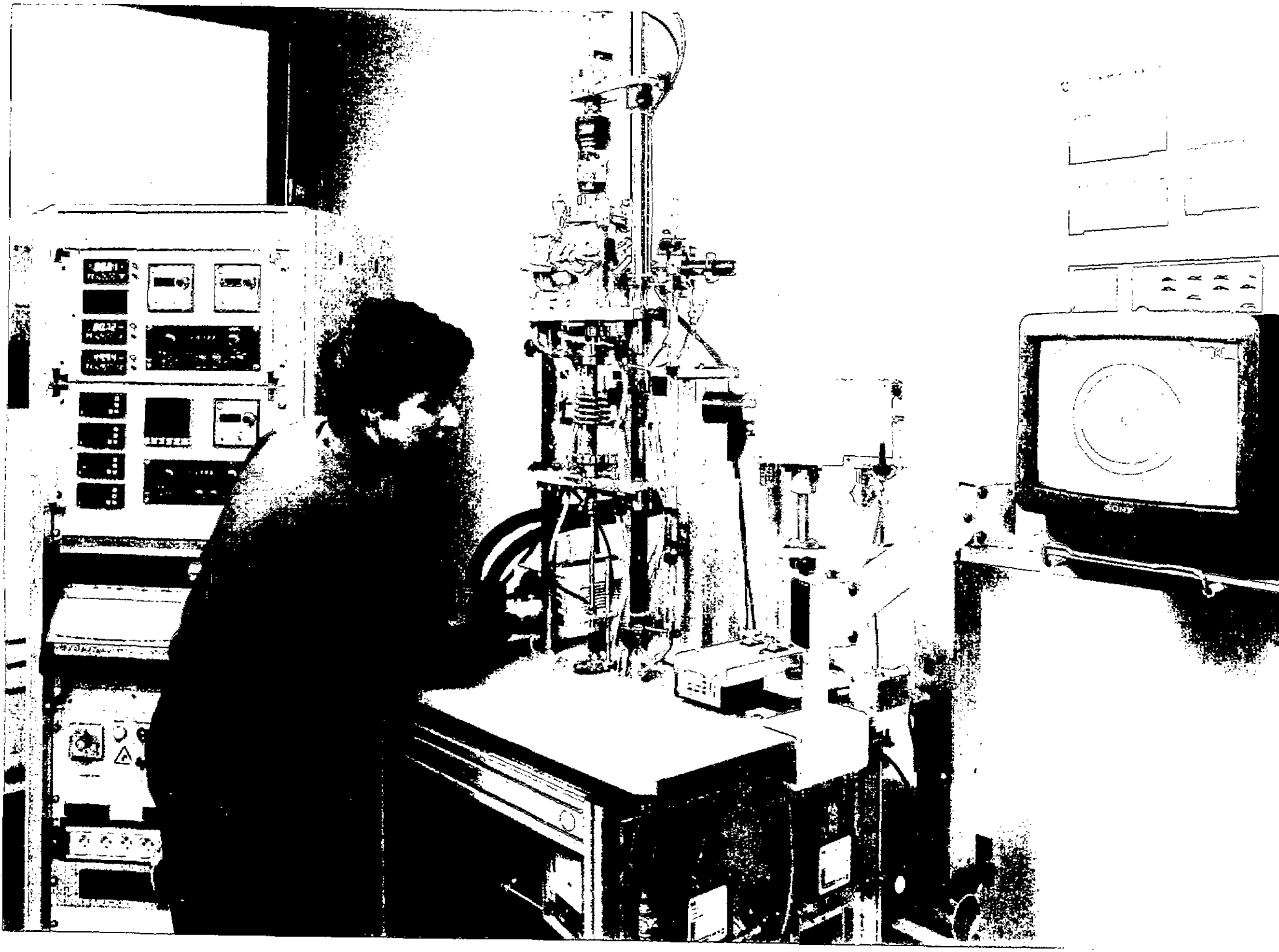
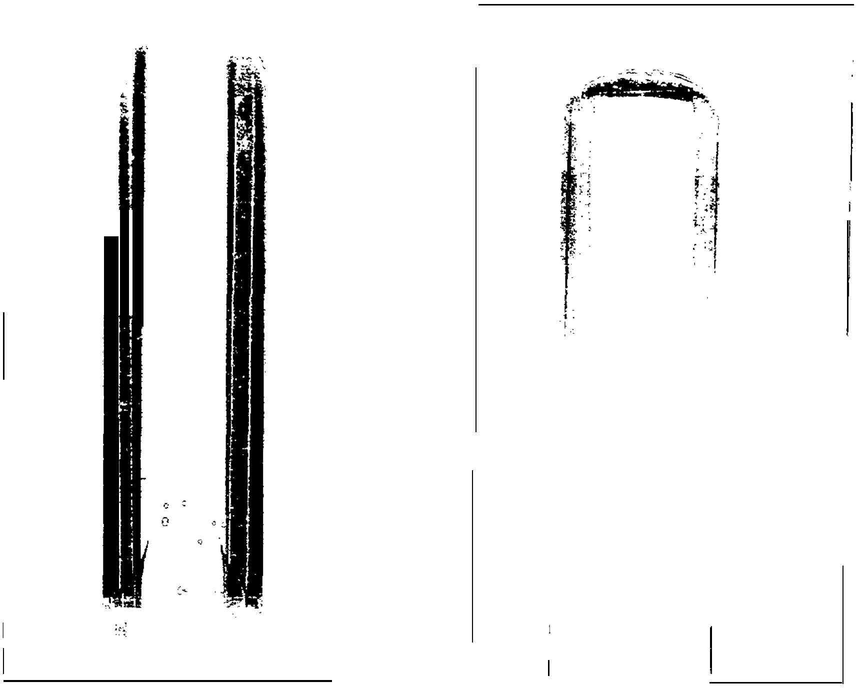


Figure 5 : Basic equipment for Vertical Tubular Levitation at CEA-CEREM.



ZBLAN Glass

AR Glass

Figure 6 : AR and ZBLAN glass rods molded in the vertical tubular levitator.

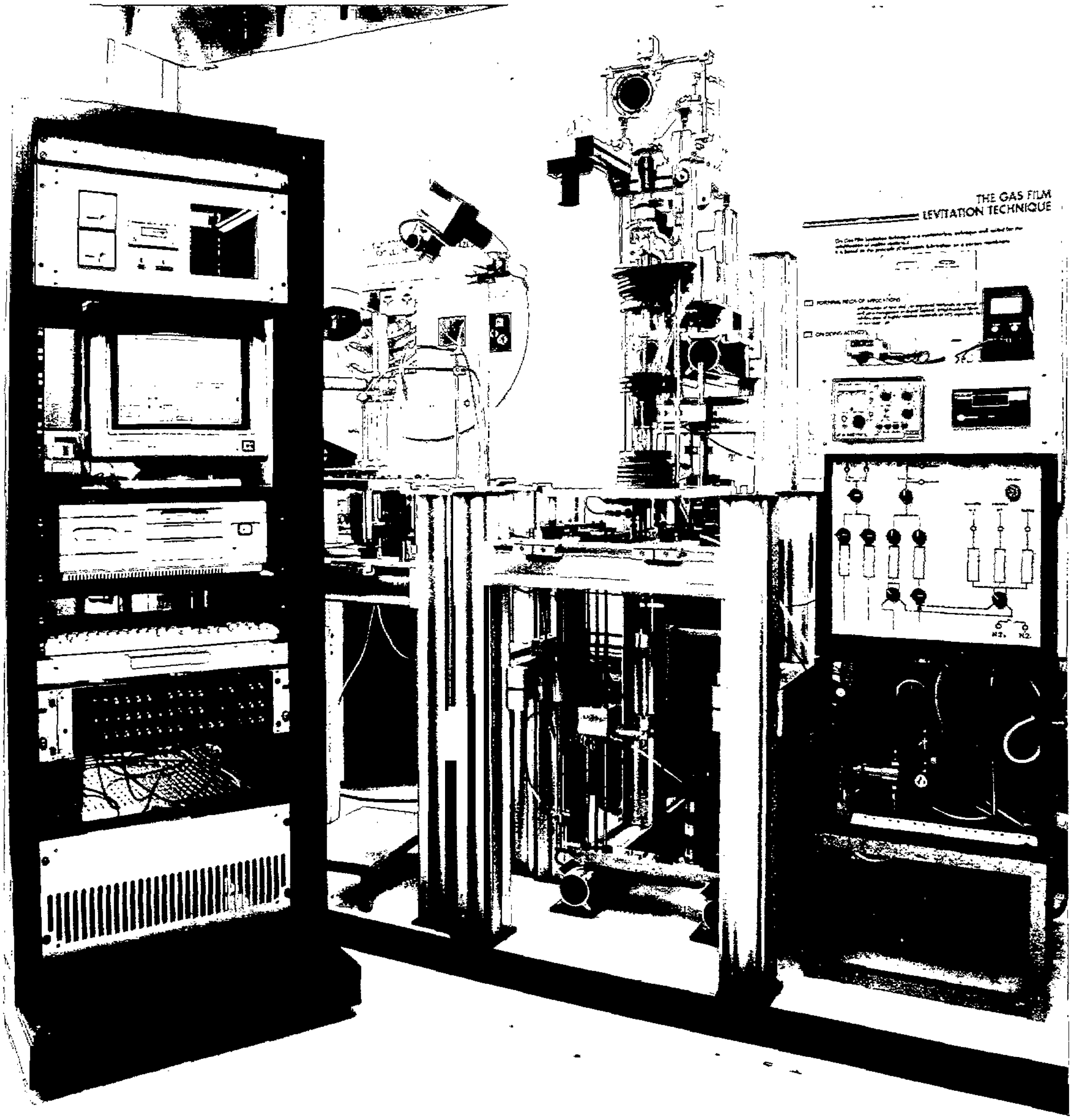


Figure 7 : View of the vertical levitator facility with continuous powder replenishment.

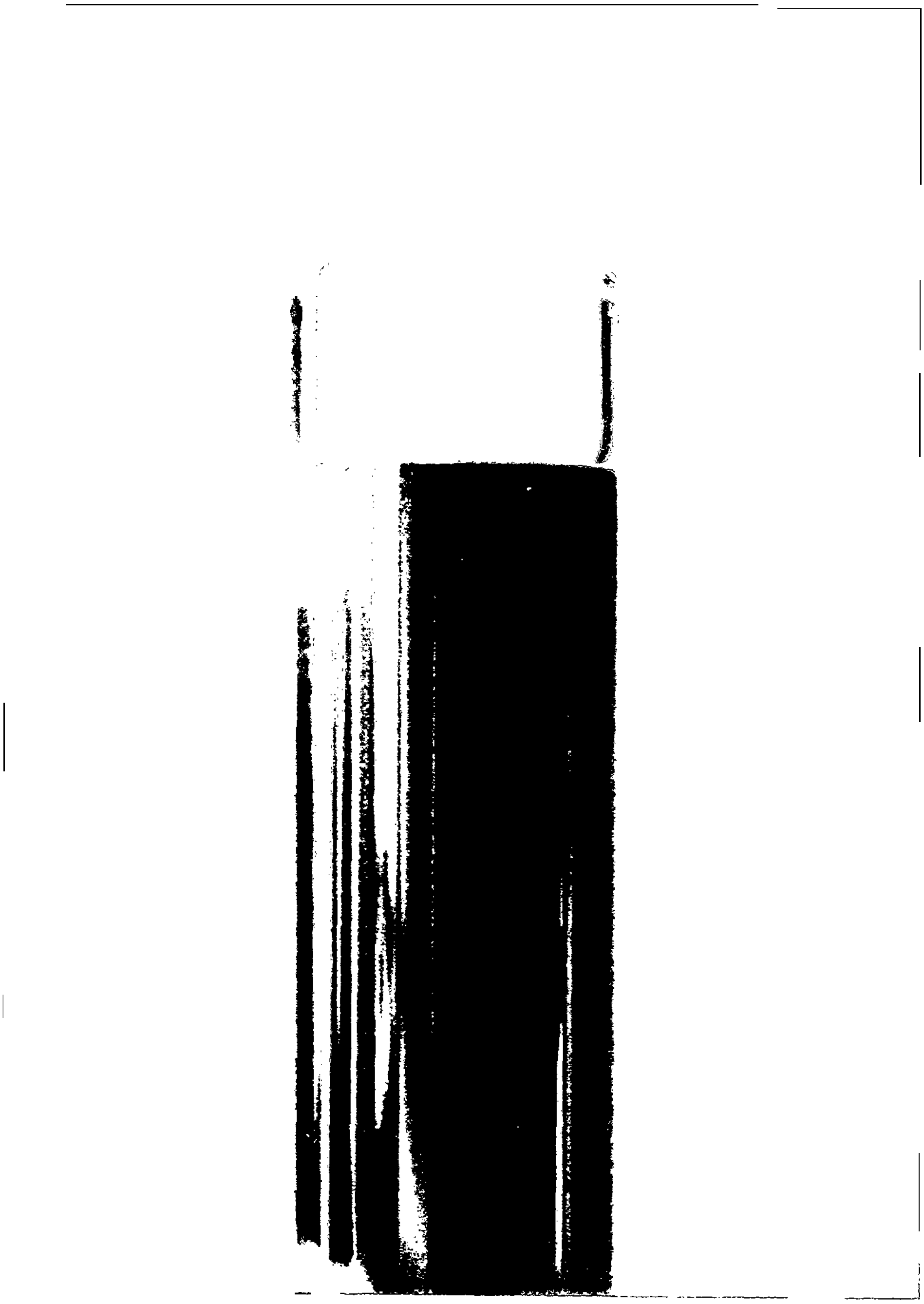


Figure 8 : ZBLAN glass cylinder recovered after levitation in the vertical levitator.

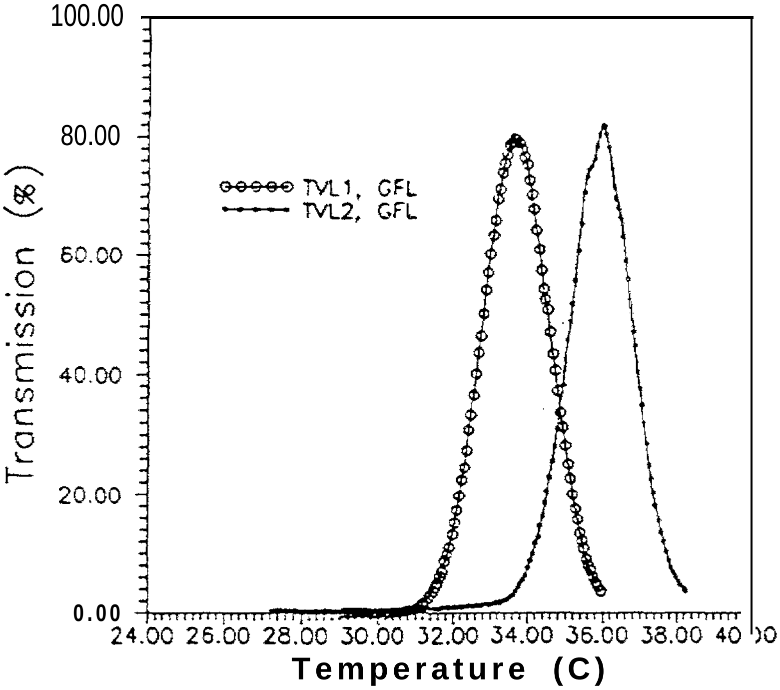


Figure 9 a) : Christianson plots of levitated ZBLAN glass samples processed in the tubular vertical levitator (liquid : tetrachlorethene).

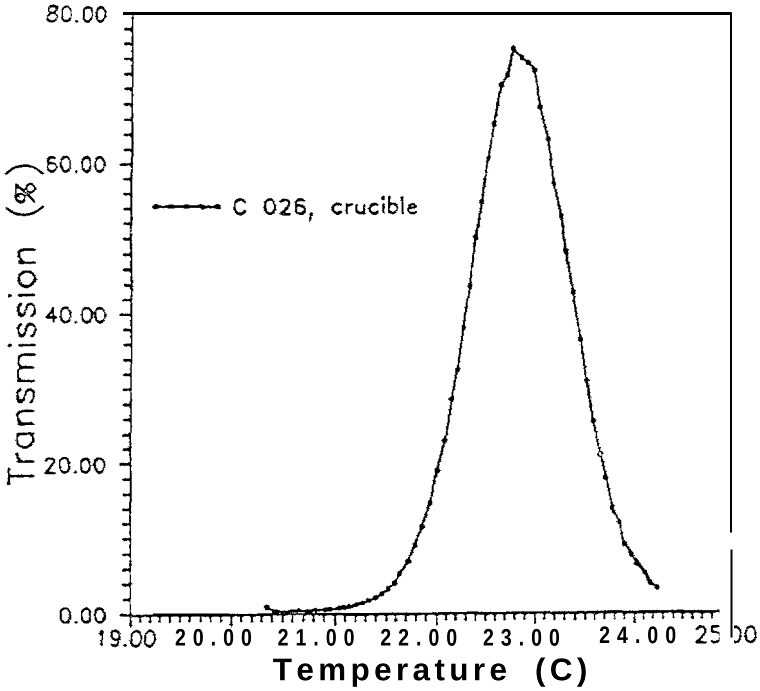


Figure 9 b) : Christiansen plot of the best ZBLAN sample produced in crucible with optimised conditions (liquid : tetrachlorethene).

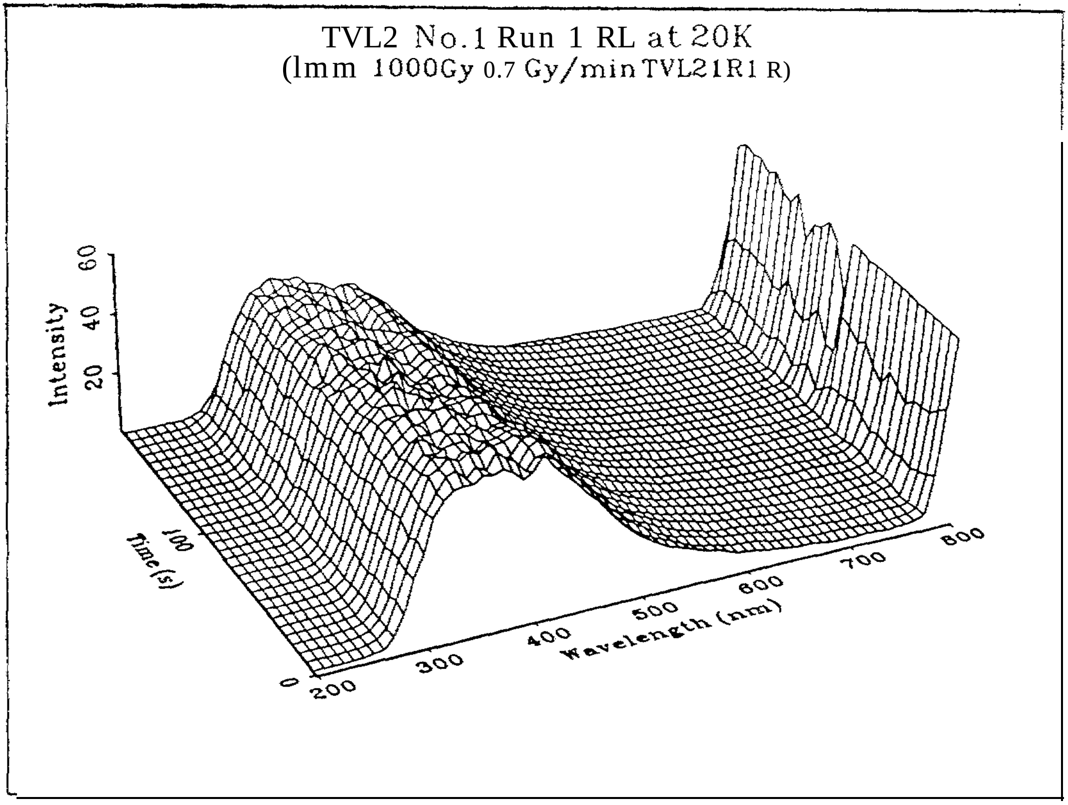


Figure 10 a) : Radioluminescence spectra of a levitated ZBLAN glass cylinder (Tubular vertical levitator].

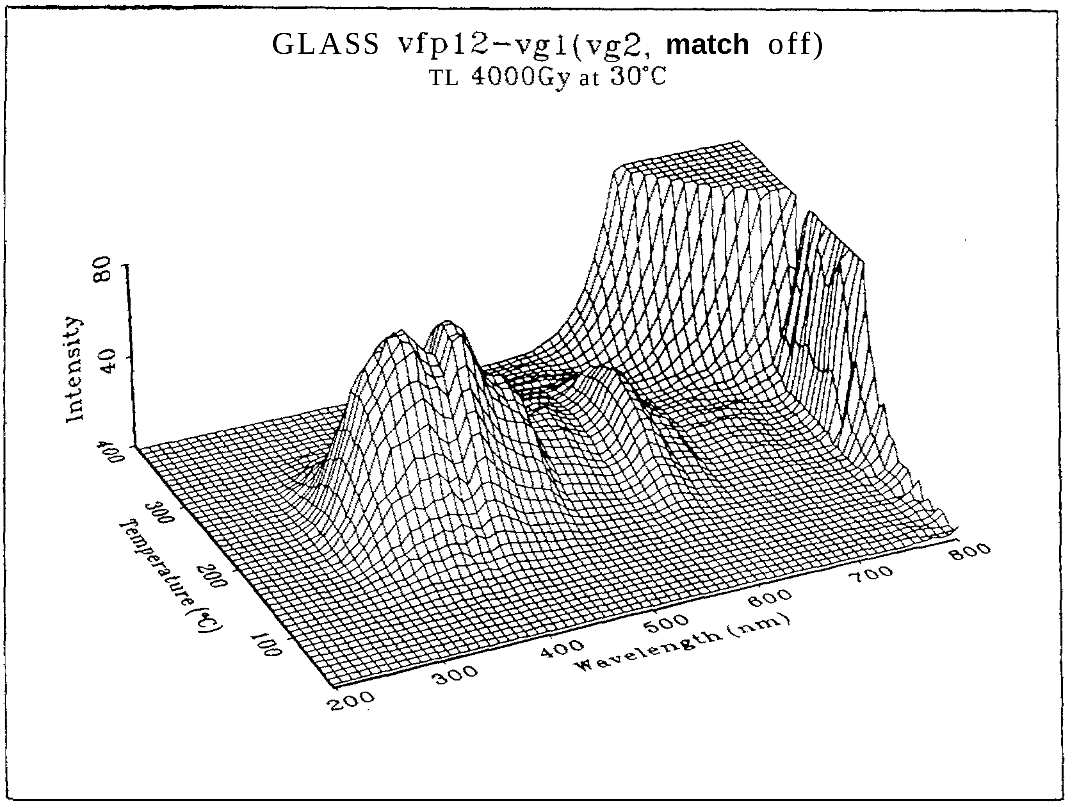
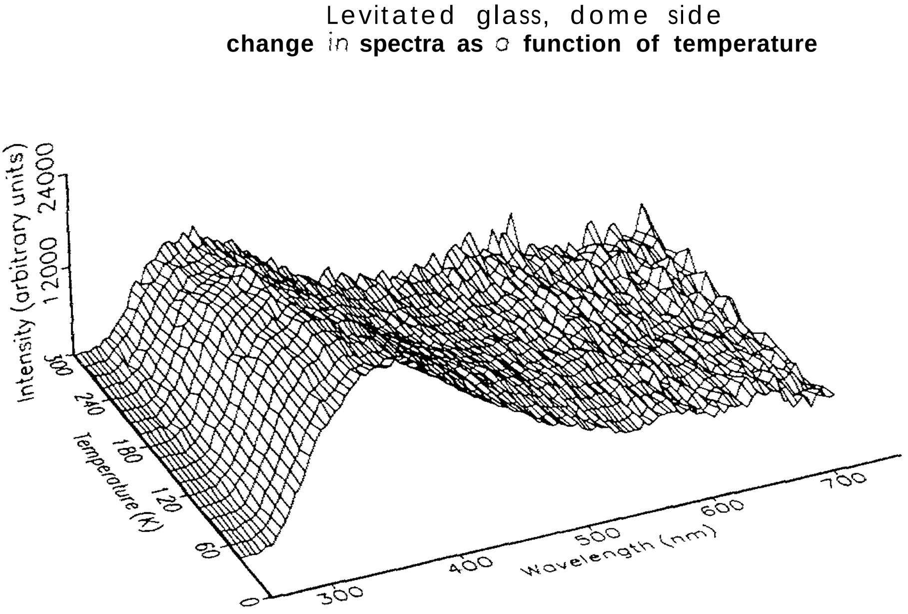
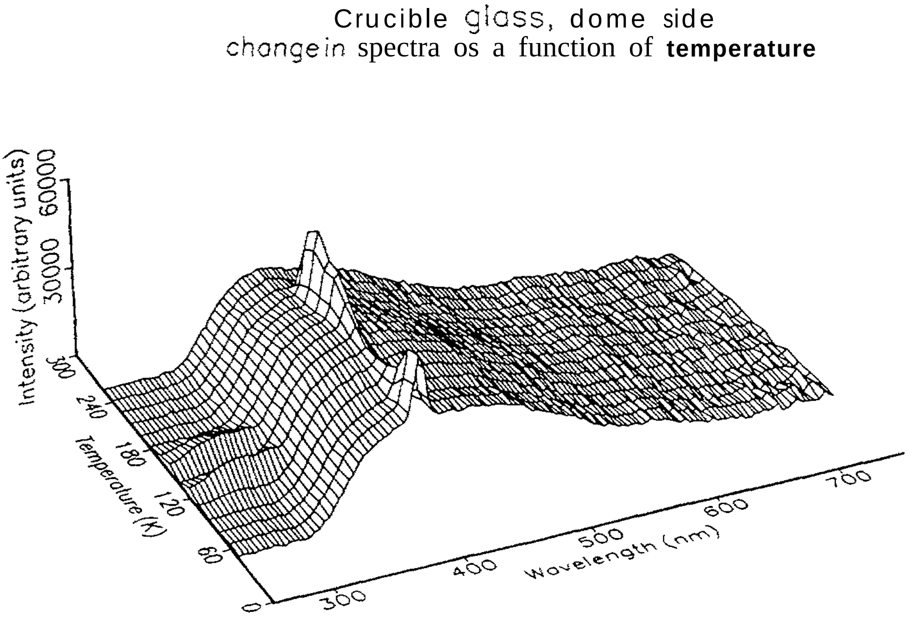


Figure 10 b): Thermoluminescence spectra of a levitated glass rod (Horizontal levitation).



<u>Figure 11 a)</u> : Cathodoluminescence spectra of the lower surface of a levitated glass disc (ZBLAN).



<u>Figure 11 b)</u> : Cathodoluminescence spectra of the lower surface of a crucible glass disc (ZBLAN).

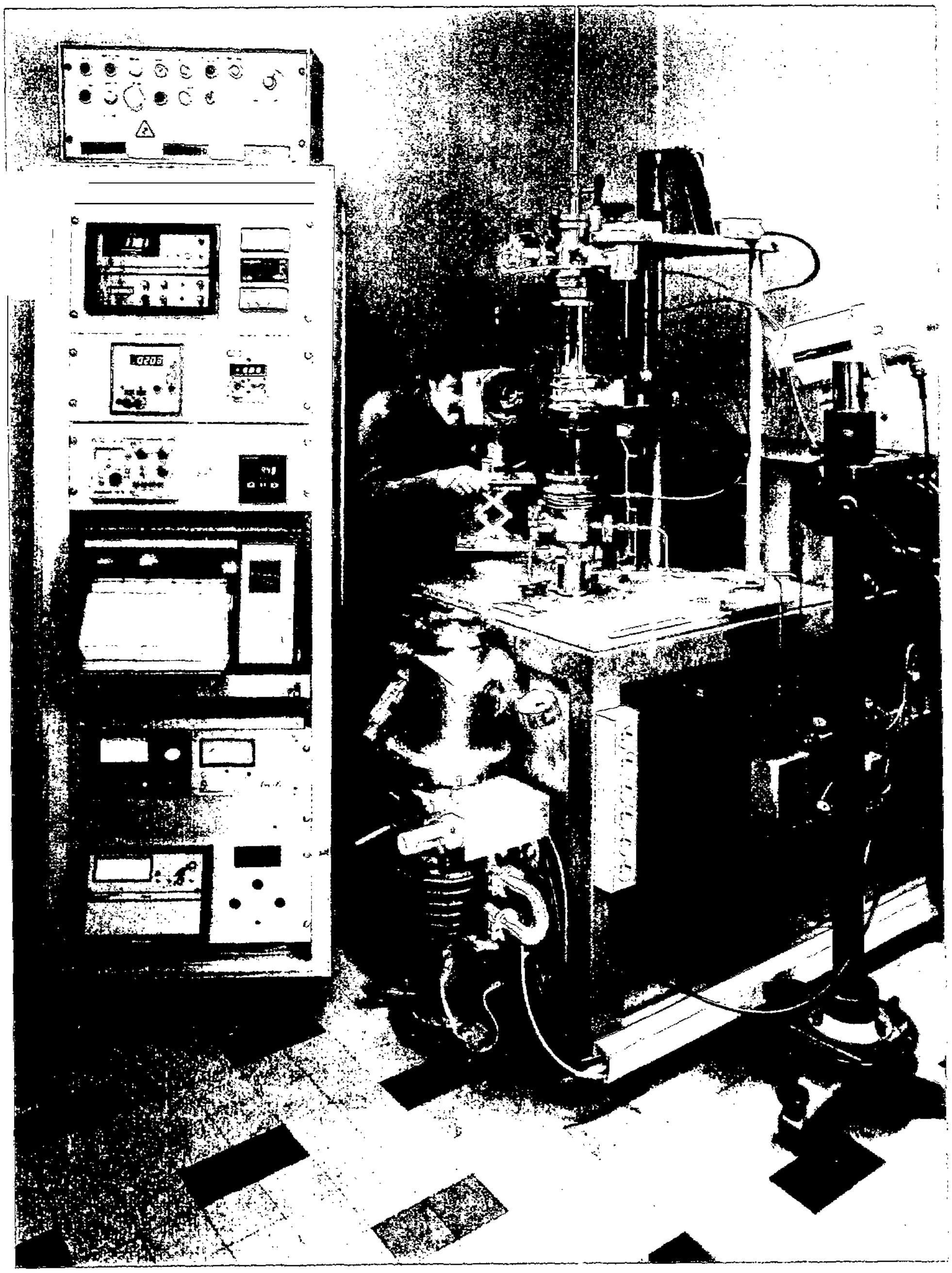


Figure 12 : Levitator "Beatrice" - Overall view.

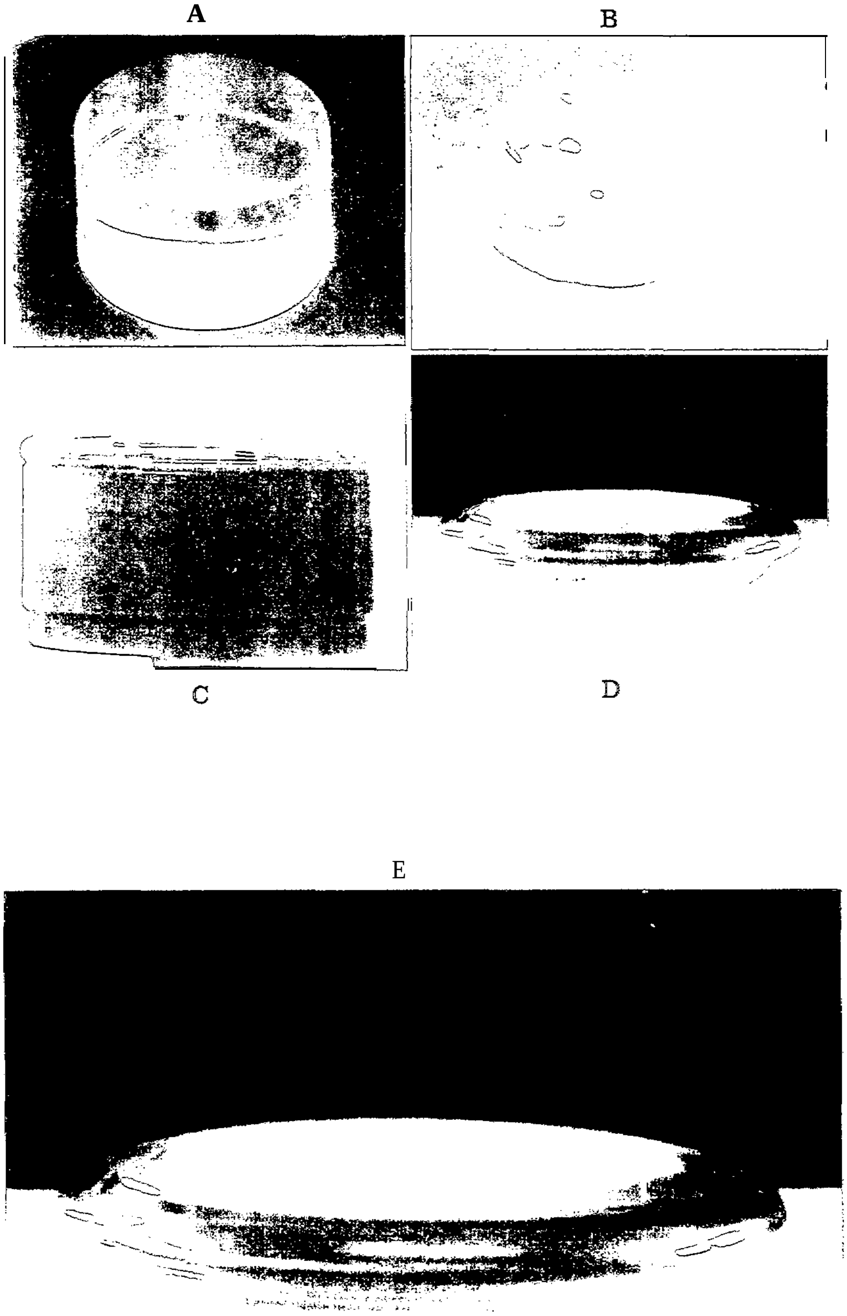


Figure 13: Large Pyrex™ glass samples containerless processed by Gas Film Levitation.

- **a** : Disc precursor sample (Dxh = 53 x 33.6 mm^2)
- **b** : After shaping in contact with diffusing element (900°C, 15 min, Argon)
- **c**, **d**, e : After GFL contactless processing (1250°C, 10 min, Argon)

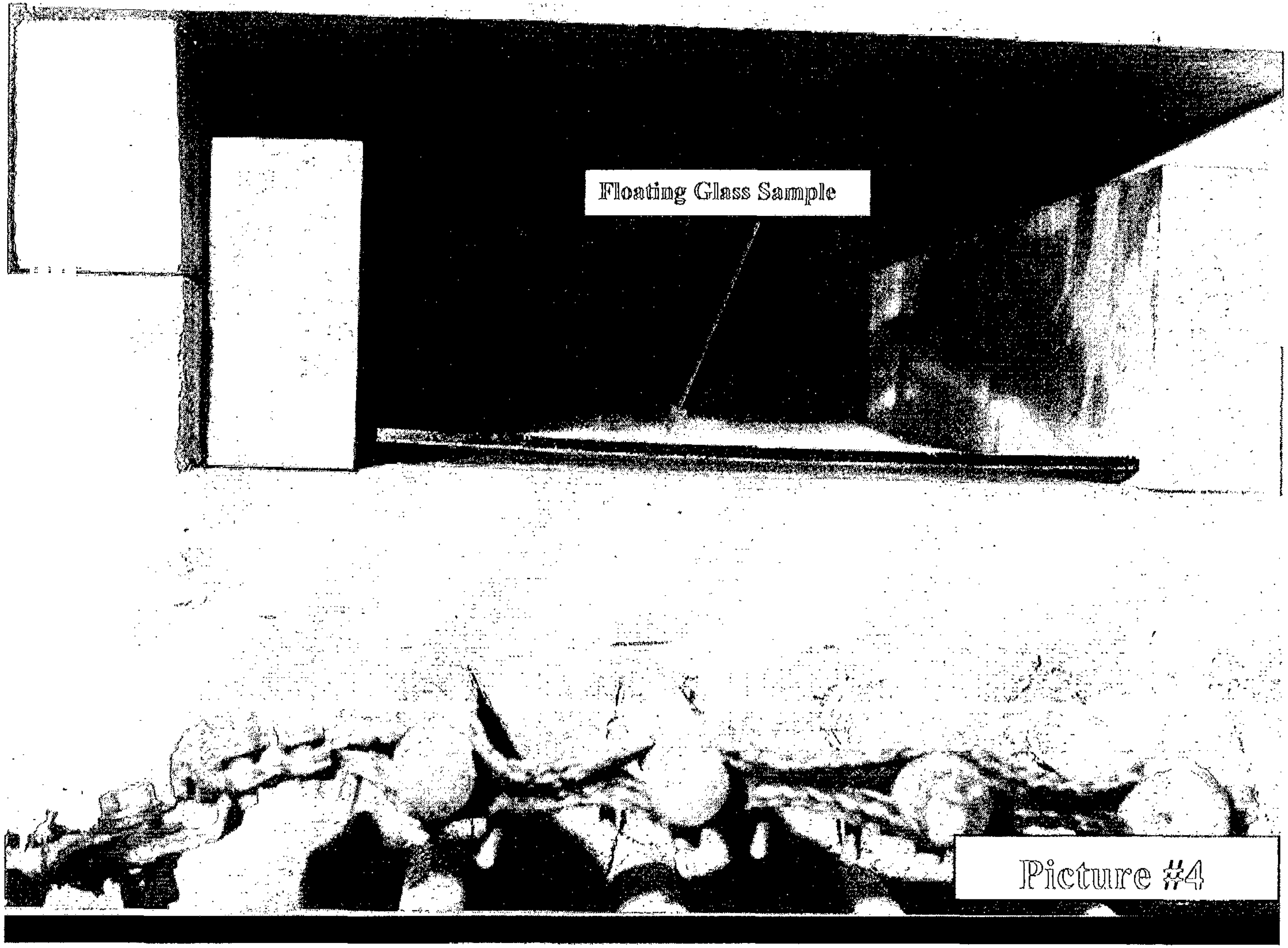


Figure 14 : View of the laboratory plant **dedicated** to the flotation of SLS glass **plates.**

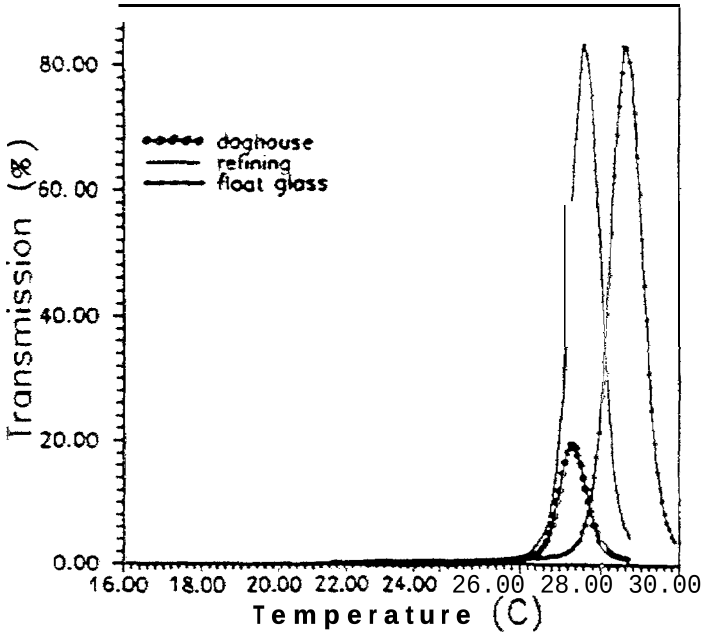


Figure 15 a) : Christianson plots of industrial SLS oxide glass samples (liquid : chlorobenzene).

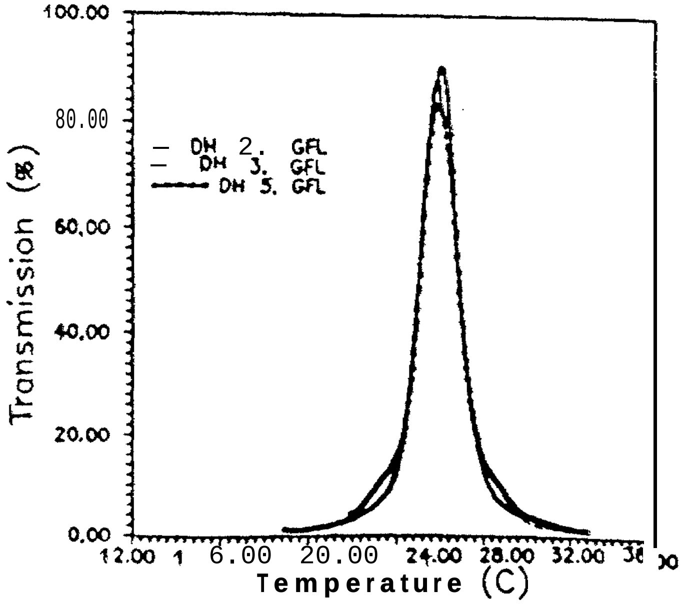


Figure 15 b) : Christiansen plots of levitated doghouse SLS samples (liquid : chlorobenzene).

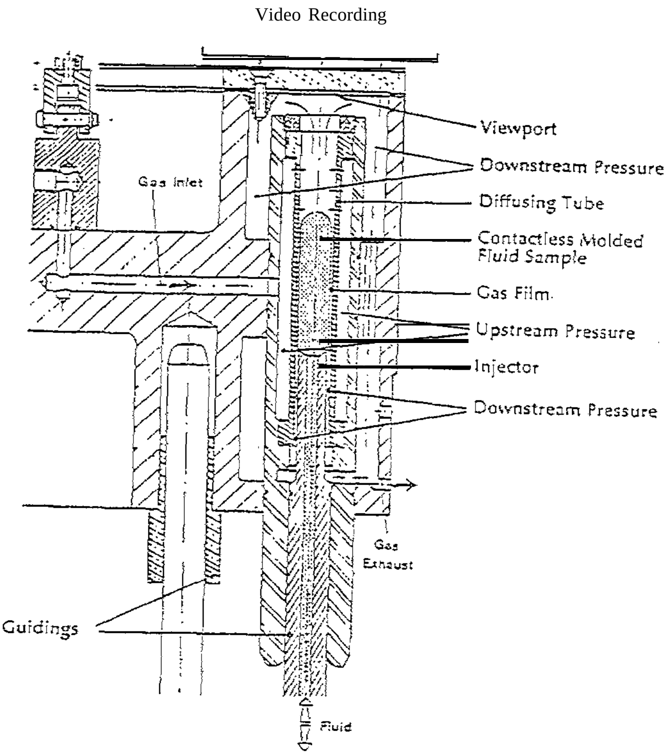


Figure 16 a) : Tubular Gas Film Levitator. Microgravity demonstration on Parabolic Flight. Test cell principle.

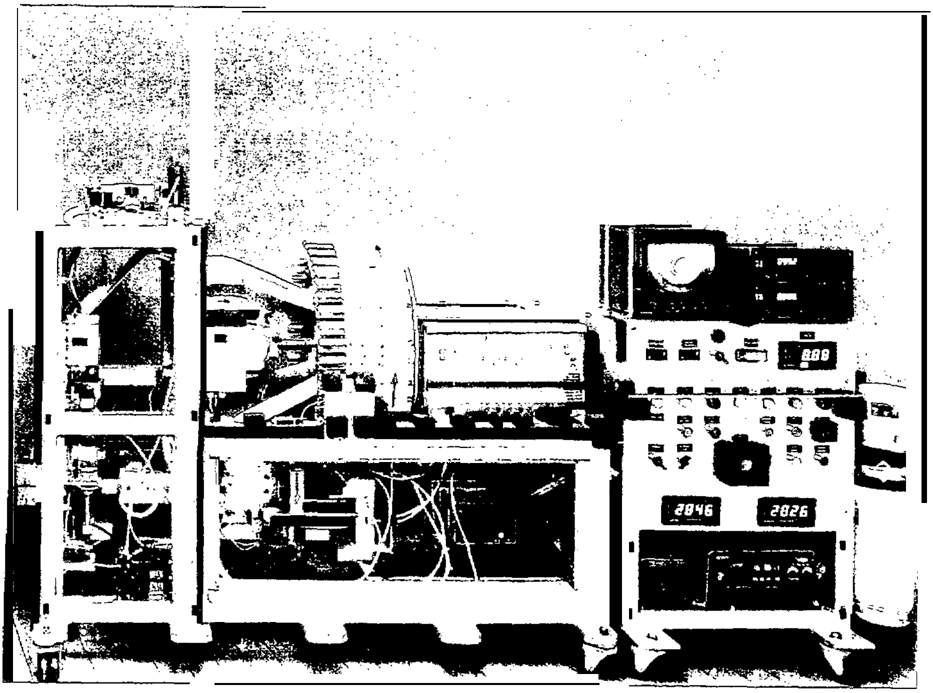


Figure 16 b) : Tubular Gas Film Levitator. Microgravity demonstration on parabolic Flight. Overall view of the test bench in Flight configuration.