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Gradient index ophthalmic glasses

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Abstract

The use of gradient index would significantly improve the characteristics and properties of optical mineral glass components, namely" ophthalmic lenses.
The goal of the research programme, founded by EC, is to design optical components and develop the corresponding materials for creating new glass lenses **with** spatially varying (gradient) refractive index (GRIN) for use in ophthalmic optics.
Design tools were developed for optimizing image properties of lenses given the refractive index profile of the glass. an optical bench was built for measuring GRIN profiles based on deflectometry principle. The equipment is fully computerized and can be used to measure index profiles of large size blanks (up to 80 mm).
Among the three material technologies investigated (Impregnation/leaching of porous preforms, Casting of colloidal glass precursors, and High temperature interdiffusion) only the last was successful in obtaining optical quality glass with refractive index variation up to 0.2. The use of the developed design tools shows that the generated profiles for axial geometry are not sufficient in shape to compete with high refractive homogeneous glasses. Further development is needed for taking full advantage of the gradient index.

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1. Introduction

Ophthalmic lenses have been greatly improved in recent years. Progress in numerical modelling and computing has been very helpful for optimizing geometry of lenses, especially of multi-focal ones. The basic design of constant refractive index lenses is now well mastered and the effort was concentrated on additional comfort properties (photochromism, reflection-free layers, . ..).
However, entirely new and exciting opportunities are attainable by using GRadient INdex materials (GRIN), in which chemical composition is manipulated to create an index variation, either across the radius (radial GRIN) or along the axis (axial GRIN). [1]
GRIN lenses can offer substantial advances over the known spherical and aspheric spectacle lenses in homogeneous materials. All monochromatic image aberrations could be fully eliminated, resulting in complete correction for all angles of view and, at the same time, the lens thickness can be pre-set.
As a result of the additional degree of freedom obtained with a combination of local refractive index variation and surface design, particularly great advances can be anticipated in the field of progressive lenses.
For ophthalmic applications the index variation zone must extend over 50 mm instead of those of a few millimeters it is possible to achieve using the current state of the art: the total change in refractive index needs to be between 0.05 and 0.3.
This combination of index range and spatial extent is only accessible by developing new fabrication processes, and the associated tools for lens design and metrology.
Studies on GRIN glasses have been carried out since 1965 and recent results have shown that suitable materials can potentially be produced by three different processing strategies [2]:
- altering chemical composition of uniform refractive index homogeneous bulk glass preforms by ionic or molecular diffusion of constituents into or out of the preforms.
- changing the molecular structure of a uniform refractive index dense preform by irradiation with neutrons, rays, UV light, laser beam or ionic implantation.
- producing a desired index profile during the fabrication of a glass preform through accurately controlling the concentration of refractive index-modifying species in successive. layers from which the preform is built up.
The aim of the project was to demonstrate an integrated design measurement and processing capability for fabricating gradient index (GRIN) lenses, mainly for ophthalmic application .

2. Technical description

The project was structured in three main research domains which were investigated in an interactive way: Lens design, Materials Technology, and Metrology.

2.1. Lens design and Metrology

In order to be in position to evaluate the ophthalmic application potential corresponding to the actual status of the GRIN Material Technology, Methods and software took were developed for establishing the best lens design for a given index profiles in both geometries i.e. radial and axial.
This was achieved by developing a universal and versatile optimization routine which allows the calculation of the ophthalmic lens properties' in the position of wear as well as the inclusion of the best esthetical characteristics.
Emphasis was given to build a general architecture of the GRIN routines, in order to insure from the begiming the ability of further modifications of the ways of representing the refractive index variation, i.e. to insure an easy maintenance of the code.
The architecture of the project has been organized in such a way that it will be easy to add a specific routine for a specific gradient refractive index, depending upon the requirements of the Materials technology. An important task of the project was precisely to be able to modelize promptly and evaluate in the sense of the ophthalmic requirements a given GRIN distribution proposed by Glass manufacturer.

To be able to qualify GRIN glass at the manufacturer locations two gradient index measurement techniques were compared; Interferometry and deflectometry. A breadboard model was built based on deflectometry for measuring large size blanks.

2.2. Technology

Among the various routes allowing to create a material with controlled refractive index gradient and taking into account the limitations and advantages of the current technologies (Figure 1) on one hand and the project objectives on the other hand, we have investigated three technical approaches able to meet the objectives of the project.

1) Impregnation and/or selective leaching of porous or gel structures.
2) Controlled casting of colloids corresponding to high refractive index glass compositions.
3) High temperature diffusion between glass compositions with different refractive index.

Figure 2 shows schematically the basic principles behind each approach.

2.2.1 *Impregnation/leaching of porous preforms*

Contrary to the well known ion exchange technology, this approach shows no other Imitation than the necessary stability of the composition formed by either impregnation or selective leaching against devitrification or phase separation during the consolidation of the porous GRIN preforms.
Ions highly contributing to the refractive index such as Ti,Nb,La,Pb,Ba can potentially be used. Since impregnation or leaching are made on high porosity materials (≥ 80 %), high An and high extent of the gradient are expected.

2.2.2. *Controlled casting of colloids.*

The overall objective of this part of the project is to produce a gradient-index material by casting successive layers of colloïdal precursors with a range of *compositions,* drying the casting and then firing to sinter the preform into a transparent glass monolith. The shorter term objective is to demonstrate that transparent glass monoliths of homogeneous composition can be created for two glasses with a suitable refractive index difference. The binary system SiO2-PbO was initially chosen but this was soon abandoned due to problems with crystallisation. We then concentrate the effort in the ternary system SiO2-K2O-PbO. Two compositions were used : 45% SiO2-10%K2O-45%PbO and 85%Si02-10%K20- 5%PbO.
The technique used to generate compositions in the colloidal state was either synthesis from Sol-gel [3-7] precursors *or* dispersed submicronic particles made by conventional milling of glass. Both techniques allows to elaborate complex glass precursors either in the form of submicronic particles or colloidal solutions of various chemistry and should give an advantage on sintering temperatures.

2.2.3. High temperature interdiffusion

Generally in an ion exchange process, monovalent cations are exchanged by external cations having lower polarizability. A gradient of refractive index is developed due to variation in the composition and distribution of monovalent cations in the preform after the exchange process,
The ion exchange takes place between the preform and a salt of the ion to be exchanged. This process is carried out at temperatures lower than the glass transition temperature and can eventually be electrically assisted. Because of the low diffusion rates, the process is very slow and limited to lengths not exceeding I mm.
The approach chosen here is a high temperature diffusion (100 to 2000 poises) process which allows an enhancement of the diffusion rates and should lead to an increase of the extent of the gradient.
The objective here was to evaluate the practical gradient which can be obtained and to what extent.
Although the final glass composition should eventually lead to a complex multicomponent glass, the interdiffusion studies have been undertaken with a model lead containing glass which makes the study easier from an experimental and theoretical point of view.
The interdiffusion process was studied as an interface reaction by contacting two or more glasses which contain the diffusing ions.

3. Results

3.1 **Lens design**

Between the bordering surfaces of an inhomogeneous glass material, the ray course is determined by a non-linear (vectorial) differential equation of the 2nd order (called ray equation) which can be transformed to [8]

$$\frac{d^2R}{dt^2} = n(R).\nabla n(R) \qquad \nabla n = \left(\frac{\partial n}{\partial x}, \frac{\partial n}{\partial y}, \frac{\partial n}{\partial z}\right)^T \qquad (1)$$

where R is the vector of position and t the independent variable.
This differential equation has the special characteristic that the 1st derivative dR/dt and the independent variable t do not appear explicitly. In this case a widely used process is the RKN process (Runge-Kutta-Nyström process) of the 4th

order [8] which provides for a step size Δt position and direction of the ray at a point $t + \Delta t$. The step size selected is orientated on the greatest change in the refractive index and is maintained even in areas of lower refractive index change. This appears to be uneconomical as every step is independent of the preceding one and as so the step size could be selected variably.

Additionally to the automated control of the step size a further problem is the ray surface intersection. A ray which is started from a point on one of the two surfaces of a lens in a certain direction and which is calculated with a numerical process will be incident to the opposite surface. If the points (R_n) and (R_{n+1}) are on different sides of this surface, then we are faced with the task of determining the point of ray surface intersection and the direction of the ray at the point of intersection with optimal precision (and computing time) [9].

Here, optimal precision means: If the process used for the ray computation is of the order of consistency 4 or 6, then the determination of the point of intersection must also be of the order 4 or 6.

The following numerical processes were compared:

RKN IP(4): RKN method of 4th order with constant step size
NF IP 4(5) : RKN method 4(5) with step size controlbyFeh]berg[10]
NF IP 6(7): RKN method 6(7) with step size control by Fehlberg [10]
RKN EX(4): RKN method of 4th order with step size doubling

The improvement of ray tracing by means of step size control and optimization of ray surface intersection produced a time saving of between 20 and 70% over ray tracing with constant step size and non-optimal methods of determining the ray surface intersection. Step size doubling can be ruled out. Which of the different procedures by Fehlberg is the most suitable will depend mainly on the thickness of the glass and the course of the index profile,

The main benefit of this time saving only unfolds its full force with non-rotationally symmetrical gradient lenses due to the incomparably larger number of rays to be traced,

optimization programs were developed within the project which can be used to determine index profiles and/or meridians of the surfaces in such a way that the lenses become "optimum" with regard to a given merit function.

The merit function is a number which is the sum of weighted squared optical defects. The result depends on the choice of suitable features with suitable corresponding weights.

The description of the profiles of the axial and radial gradients and the meridians of the front or back surface were carried out with Taylor series expansion, conic sections with additional terms and B-splines.

The possibilities for improvement over homogeneous glass materials can be found primarily in:

- A reduction in the critical thickness, i.e. the centre thickness for positive power lenses and the rim thickness for negative power lenses;
- A correction or reduction of the most significant imaging errors, i.e. astigmatism and refractive en-or; and
- Possibly, a correction or reduction of chromatic aberration.

A systematic classification of the possibilities of a lens with radial or axial gradient is based on which of the three determinant factors, i.e. front surface, back surface and index profile, are given and which have to be found, The two most important cases here are:

- The external shape of the lens is given and the index profile has to be found
- The index profile and one surface are given and the other surface has to be found.

The effect of an axial or radial gradient regarding the reduction in critical thickness can be discussed most easily by means of the vertex power formulae. For example, the vertex power S'_{ax} of an axial gradient can be described by the approximation formula in three ways

$$S'_{ax} \approx \frac{n_1 - 1}{R_1} - \frac{n_2 - 1}{R_2} = (n_1 - 1)(\frac{1}{R_1} - \frac{1}{R_2}) + \frac{n_1 - n_2}{R_2}$$

$$= (n_2 - 1)(\frac{1}{R_1} - \frac{1}{R_2}) + \frac{n_1 - n_2}{R_2}$$

where n_1, n_2 are the refractive indices at the vertex of the i-lent surface resp. back surface and R_1, R_2 are the radii of curvature at the same vertices.

This description shows directly that the vertex power increases if $n_1 - n_2 = Dn > 0$ applies, irrespective of whether a comparison is made with an homogeneous glass of index n_1 or n_2. .The decreasing index from the front surface vertex to the back surface vertex cannot only be used to increase the vertex power, hut with the same vertex power the spherical front surface of a positive lens can also be made flatter and thus the centre thickness reduced. Compared with the effect of a radial gradient, however, these reductions in thickness are low.

An analogous comparison applies for a reduction in the vertex power if $n_1 - n_2 = Dn < 0$
$\Delta n = 0$ means that the whole area between the vertices is homogeneous. In this case no thickness reduction can be made with spherical 'surfaces. A correction of the imaging errors is only possible with a suitable profile to the right of the back surface vertex.

In all 3 cases . $n \gtreqless 0$ fairly high reductions in thickness can only he obtained with an aspheric surface design. The large imaging errors which can arise due to an aspheric surface design require correspondingly high index changes.
The optimization routines and merit functions meet the demands made on them of determining the free parameters of the meridians of front and back surface and of the index profile in such a way that the lens becomes optimal with regard to a predetermined merit function.
In particular, the investigations showed which axial or radial profiles would be required to substantially reduce the maximum thickness of a homogeneous (spherical or aspheric) spectacle lens of equal power and comparable imaging properties.

3.2. Metrology

Interferometric and deflectometric transmission measurements can be used to analyze the wavefront deviation due to the Grin samples. From this wavefront deviation the index distribution could be calculated via a ray tracing method
For thick samples and reasonable high products of A n*e (e being the thickness in the gradient direction) it is preferable to work with one transmission pass through the sample,
One single transmission pass is possible in Essilor's deflectometer and the Mach - Zehnder interferometer, The deflectometer principle is however preferable. The optical and optomechanical set-up is simply built and insensitive to environmental effects. It has the advantage of a tunable sensitivity of the system and a huge dynamic measuring range that is typically one order of magnitude higher than in the existing Mach - Zehnder interferometer.
The deflectometer principle was therefore chosen and a practical instrument was built.
A schematic description of the optical bench for the deflectometer is given in figure 3. The breadboard model was constructed and all associated tools leading to automatic measurement of the map of index distribution developed. The software operating the deflectometer was adapted from an existing Essilor's code.
A view of the built equipment is given in figure 4. The equipment measure refractive index distribution only with I wavelength (633 rim). Color dispersion map should be included in future development.
The refining of the experimental deflectometer and the specification of the final instrument for a production environment has to be made after checking with prototype grin lenses.

3.3. Materials Technology

3.3.1. impregnation/Ieaching

Three different techniques were invest igated for impregnation :

* Liquid impregnation
* Chemical vapour
* Nebuli sed aerosol

Only the first of these techniques has resulted in doping levels capable of being produced within a commercially acceptable timescale. Silica and Silica-potassium porous preforms were manufactured according to [11]

a) Chemical vapour technique

The chemical vapour impregnation technique has been of limited success. The problems stem from the reactivity of the vapour produced (precursores : Ti(OR)4) which precipitates on contact with the preform surface.This precipitation formed an effective barrier layer preventing ingress of vapour into the preform.
Many variations were attempted., none of which resulted in major improvements in the doping levels achieved. As further modifications to drastically improve the procedure were not identified, the investigations into this processing route have been abandoned early in the project.

b) Nebulised spray impregnation

The nebulised spray impregnation technique had an inherent limitation in that it would be difficult to produce a radial concentration gradient.
Only very dilute nebulised vapors were possible due to experimental constraints and hence the doping levels achieved were low, To build up an acceptable doping level would require excessively long operational time.
This technique was therefore also abandoned in favour of the more successful liquid impregnation technique.

c) Liquid impregnation

Liquid impregnation has proven to be the most effective procedure for impregnating the preforms with lead salts in the range desired to achieve the gradient of refractive index required. It was evident from initial studies that the capillary forces within the preforms were not enough to infiltrate lead salts into the center of the preform. Therefore it has been necessary to evacuate the preforms plier to impregnation and use solvents of lower surface tension.
All homogeneously impregnated silica preforms with lead salts crystallized or "foamed" during sintering, due to emprisonment of decomposition by products. Binary preforms were then used with the following characteristics.

Preform A : Composition 26 wt% K_2O, 74 wt % SiO_2 with 80 % of porosity

This preform type has been used for the majority of impregnation and leaching studies
The advantage of this preform is its' greater pore diameter making it easier to impregnate and is less likely to fragment due to surface tension effects. The unimpregnated preforms were prone to crystallisation during sintering.

Preform B . . Composition 12 wt% K_2O, 88 wt% SiO_2 with 65% of porosity

These samples had a finer pore size than preforms A. The weight gains resulting from impregnation with Lead (II) Acetate were lower than those measured for the preforms A. Also, they had a tendency to fragment on immersion into the impregnation liquor even at atmospheric pressure.
Their main advantage was that they could be more easily sintered to a transparent glass.

<u>Development of the concentration gradient</u>

The aim of this stage is to develop a concentration profile by leaching either axially or radially across the homogeneously lead impregnated preform.
For radial gradients a holder was built so that the leaching solution was only in contact with the circumference of the preforms when they were immersed. For axial gradients the circumference *and one* of the faces of the cylinder were masked by the holder to expose only one face,
The samples were immersed in the leaching solution (Acetic Acid) for various times after which the samples underwent the fixing procedure as outlinedin[12]

Radial Gradients

The profile of lead concentration generated in the A lead impregnated preforms is shown in Figure 5. This figure shows an unleached profile and the modification of this profile achieved after different leaching times. This shows that the longer the leaching time the flatter the concentration profile becomes.
This suggests that a Δn of 0.12 is theoretically possible using this process. These compositions all lie within the glass forming region of the K_2O, PbO, SiO_2 tertiary system .

Axial Gradients

The profiles for an unleached and axially leached (1 hour) B preform are shown in Figure 6. The figure shows a steep gradient measured across the preform. These compositions also lie within the glass forming region of the tertiary system.
Radial and axial composition gradients could be easily prepared by this technique. It was however difficult whatever the thermal schedule used to densify them in glass of optical quality.

3.3.2 **Colloidal Casting**

Two compositions, 5%PbO-10%K_2O-85%SiO_2 and 45%PbO-10%K_2O-45%SiO_2 which have a refractive index difference of 0.1 were selected for preparation. Sols were prepared from 0X50 and double-dispersed 0X50 while lead oxide was derived from either lead nitrate or the Pb-EDTA complex; potassium oxide was provided by the nitrate or acetate salt.

Attempts to prepare transparent glasses in the ternary system by sintering at low temperature (~Tg) gels were unsuccessful. Compositions conjoining 45% PbO melted at 670°C and formed a glass. Carbon formation and decomposition of salts near the melting point caused bloating and discoloration Gels with 5% PbO were opaque with evidence of phase separation when fired at 1000°C. Gels were glassy with coarse porosity when fired at 800 or 900°C. Although bloating in the system 45%PbO-10%K_2O-45%SiO_2 was reduced by vacuum sintering gels, gas evolution due to salt decomposition near the glass melting point ruled out the possibility of preparing a low melting point glass from sols. Even sintering the monolith derived from potassium silicate caused bloating due to resorption of adsorbed H_2O even though nitrate salts and their decomposition products were absent from the gels. It was considered that optical glass in the ternary system could not be produced from casting SOIS.
In order to avoid salt decomposition during densification, glass submicronic powders were used to check the validity of the concept. Glass powder suspensions showed a large increase in viscosity when its pH was reduced from 11.6 to 5.0 suggesting agglomeration of particles was occurring. Optical quality glass could not be obtained by vacuum sintering. Glasses were translucent and opaque and bubbles were often present; use of a surfactant to modify the suspension viscosity did not eliminate the presence of bubbles in the sintered glasses. Crystal nucleation on the surface of original powder particles was the main cause of light scattering in the sintered glass. A model of the viscous sintering process was developed and confirmed that pores in castings made with <50 m powders should sinter if heated at 0.1°C per minute to their softening points assuming no trapped gases are present. Transparent glasses could not be produced by hot isostatic pressing of glass powder and crystallisation was the principal cause of opacity.

Transparent glass was successfully produced by hot pressing a soda-lime glass powder by using a clean powder, a 1 150°C pressing temperature and low-pressing pressure (1 to 10 MPa) although some bubbles remained. However, full-sized pieces of good quality glass could not be prepared

3.3.3. High Temperature Diffusion

The model glass systems for the high temperature diffusion were K_2O-PbO-SiO_2 and K_2O-PbO-Al_2O_3-B_2O_3-SiO_2. It is possible to develop an optical glass based on these glass systems by adding other components and substituting PbO by BaO, La_2O_3, etc.
The maximum PbO concentration difference was 32 mol%, which is equivalent to a refractive index difference of 0.22. The polished surfaces of (wo base glasses were contacted to form an interface with a step composition profile
Interdiffusion was studied in the range 1100 °C < T < 1500 "C. The diffusion occured normal to the interface and generated "S" shaped concentration-distance profiles as shown in Figure 7. In an infinite couple the dimension of the base glasses along the diffusion direction are large so that the composition of their ends are not influenced by diffusion in a finite time.
Interdiffusion experiments at low temperature (T < 850 °C) failed, because the glass samples always crystallized.
The concentration-distance profiles of the fused glass couples were measured with electron probe techniques. Point analysis with a step size of 200 µm at the edge of the profile and a step size of 50 µm in the middle of the measured profile was made.
At temperatures between 1100 °C and 1400 "C the concentration- distance profiles showed no influence of convection. At 1500 °C the samples were mixed by convection.
In the K_2O-PbO-Al_2O_3-B_2O_3-SiO_2 system the curvature of the areas with the same refractive index showed a strong temperature dependence. At 1100 "C the measured PbO concentration perpendicular to the diffusion direction shows no curvature (Figure 8a). The irregularities at the left side of the profiles for 2 h and 4 h are caused by bubbles at the edge of the glass. At higher temperatures a curvature is considerable (_Figure 8b). At 1400 °C this curvature reaches a maximum. This increasing curvature could be caused by the strongly decreasing surface tension of the top glass with the high B_2O_3 content. In most cases the profiles between 2500 µm and 7500 µm are not influenced by the edges.
The kinetics of the diffusion can be described with the effective binary diffusion model, which requires only one diffusion coefficient for the description. Because of some limitations of this model it cannot be used in all cases.
As an example Figure 9 shows the effective binary concentration dependent diffusion coefficients for a glass couple of the system K_2O-PbO-Al_2O_3-B_2O_3-SiO_2.
The effective binary diffusion coefficients can be used to determine the annealing conditions for such multilayer glasses. Figure 10 shows the dependence of the diffusion time and the layer thickness on the temperature.
By careful selection of glasses compositions and diffusion parameters (T,t) index variation up to 0.2 and extent up to 12 mm was demonstrated. Typical examples of profiles obtained in 40 mm diameter samples are shown in figure 11.

The high temperature interdiffusion process has the property of being transferred asymptotically **on** both sides into the homogeneous zones of the base material.
A relatively simple mathematical fiction for the axial gradient which demonstrates this asymptotic transition and which is, in addition, still sufficiently flexible, is

$$n(z) = n_{h2} + \frac{n_{h1} - n_{h2}}{(1 + e^{c(z-d)})^m} \quad (4)$$

Where:

n_{h1} Index of the 1st homogeneous base material (= value of the left asymptote)

n_{h2} Index of the 2nd homogeneous base material (= value of the right asymptote)

c,d and m are parameters which determine the "length", the "position" and the "shape" of the transition between the two asymptotes. Depending on whether $n_{h1} < n_{h2}$ or $n_{h1} > n_{h2}$ an increasing or decreasing profile is produced.
These double asymptotic functions are very useful for model calculations and can sometimes also be sufficient to demonstrate the measured index profiles. In the latter case, the 5 parameters of equation (4} are determined in such a way that, for example, the square sum of the deviations will be a minimum.
If the basic materials are given then only the 3 parameters c, d and m can be varied. ("ideal" profile with given asymptotes).
If the profile of a finished glass block is known, then the only degree of freedom for the optimisation is parameter d which determines the position of the profile with regard to the lens, i.e. the lens can still be moved as desired in the profile in the direction of the z axis. If an optimized gradient lens with spherical surfaces is compared with a homogeneous lens with an aspheric sulfate, then the result depends on the index of the homogeneous lens. If the comparison is with the highest index occurring in the profile, that is (he index of the upper asymptote, then the homogeneous lens is better for *a* positive power, as the upper part of the profile is not present in the optimized gradient lens. For a gradient lens with negative power and spherical surfaces, the reduction in the rim thickness and the correction of the imaging errors would require opposite profiles so that no improvement is possible for this reason.
Ifa gradient lens with an aspheric surface is compared with a homogeneous lens with an aspheric surface whose index corresponds to the highest occurring in the profile, then no improvement can be found in the inhomogeneous positive lens despite the asphere, while with the negative lens, slight savings in thickness are possible.
Numerical examples are given in Table I and H.
To summarize, an axial index course with 2 asymptotes and so one point of inflection means a certain limitation over a generally axial course as the point of inflection often proves to be an irritant in the optimization and is pushed out of the lens. A comparison with a homogeneous lens which index corresponds to the highest occurring in the profile is then usually unfavourable for the axial gradient lens.

4. Conclusions

Different methods of ray tracing routines were developed and checked for calculus accuracy and computer time optimization.The optimal method found to be dependent of the retractive index profile and the glass geometry. A 70% of computing time save was achieved with the optimal methods.
The *optimization routines and merit functions* meet the demands made on them of determining the free parameters of the meridians of front and back surface and of the index profile in such a way that the lens becomes optimal with regard to a predetermined merit function.
In particular, the investigations showed which axial or radial profiles would be required to substantially reduce the maximum thickness of a homogeneous (spherical or aspheric) spectacle lens of equal power and comparable imaging properties.
The different available methods (*interferometric, deflectometric*) for measuring the gradient index of such materials have been evaluated and the experimental measuring conditions determined.
Interferometric and defl ectometric transmission measurements can be used to analyze the wavefront deviation due to the GM samples. From this wavefront deviation the index distribution has to be calculated via a ray tracing method Compared with the interferometer the deflectometer has the advantage of a tunable sensitivity of the system and a huge dynamic measuring range that is typically one order of' magnitude higher than in the existing Mach - Zehnder interferometer. *The deflectometer principle was chosen and a practical instrument was built.*
Among the different *impregnation techniques (Liquid, Vapor, Aerosol infiltration)* used to load the developed porous preforms, with high refractive index ions such as Pb2+, *only the Liquid impregnation has resulted in doping levels capable of being produced within a commercially acceptable timescale.*
Procedures for Impregnation Leaching and Fixing of the concentration profiles of Lead across the preforms have been established.
Although these processes need further optimisation (Profile shape control, maximum achievable doping level, other stabilizing chemical species], *the potential of this system to generate a large Δn either in axial or radial geometry has been demonstrated. The* main difficulty in ibis approach was (he lack of *a [ethical solution to overcome the problem of crystallisation/b loating of the samples during sintering.* Optically clear samples have been demonstrated only for

binary homogeneous compositions.

It was not possible to prepare dense single phase transparent glass in the $PbO-SiO_2$ system by casting from sols as glasses were opaque and porous. It was also not possible to produce sintered optical glass in the $PbO-K_2O-SiO_2$ system by casting sols. Salt decomposition caused bloating while carbon residues produced discoloration. Optical quality glass could not be obtained by vacuum sintering powders; glasses were translucent or opaque and contained bubbles. Opacity was due to crystal nucleation on the glass powders. Transparent glasses could not reproduced by hot isostatic pressing. ***The interdiffusion technique was the most successful among th e materials technologies.*** The study was conducted in static condition with a bi layer arrangement. The main diffusing element was Pb2+ and the counter ion K+. Two model glass composition was developed; SiO2-K2O-PbO and SiO2-B2O3-Al2O3-K2O. Diffusion coefficients and activation energy for the process were calculated and help to define a continuous process for grin glass in both axial and radial geometries.

Samples of 40 mm diameter were prepared in stat ic conditions and characterized for index gradient *An index variation from 0.05 to 0.2 has been demonstrated for axial geometry. The extent of the index variation goes from 1 to 12 mm.*

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References

1. E.W Marchand "Gradient Index Optics" Academic Press, NY, 1978
2. "Topical meeting on Gradient-Index Optical Imaging systems" May 4-5, 1981 Honolulu Hawaii
   "Gradient-Index Optics" ed. D.T. Moore, SPIE vol MS 67, 1993
3. C J Brinker and G W Scherer. Sol-Gel Science. The Physics and Chemistry of Sol-gel Processing, New York, Academic Press, 1990.
4. D L Segal. Chemical Synthesis of Advanced Ceramic Materials, Cambridge University Press, 1989.
5. M Yamane. In 'Sol-Gel Optics'. Processing and Applications, edited by L C Klein, Kluwer Academic Publishers, p391, 1993.
6. T M Che, M A Banash, P R Soskey and P B Dorain. In 'Sol-Gel Optics'. Processing and Applications, edited by L C Klein, Kluwer Academic Publishers, p373, 1993.
7. E M Rabinovich. J. Non-Crystalline Solids, 63, l 55, 1984.
8. Sharma, A., D.V. Kumar, A.K. Ghatak: Appl. Optics21, No.6,984-987, 1982.
9. Stone and Forbes: J.Opt.Soc.Am.A./Vol./,No.2/February1990
10. Fehlberg, E.: Computing 10,305-31 5, 1972.
11. R.D. Shoup W.J. Wein US Pat. 4,059,658, 1977
12. M. Yamane & all "Gradient index glass rods prepared by the sol gel process J. Non Cryst. Solids N" 100 506,1989

Figure captions

Figure 1 :State of the art of Material Technologies and project objectives

Figure 2 : Approaches for Grin Technology

Figure 3 :Grin deflectometer. Description of the optical assembly

Figure 4 :View of the built Grin deflectometer

Figure 5 :Radial PbO profile after leaching of an A porous preform.

Figure 6 :Axial composition profile after leaching ofa B porous preform

Figure 7 :Typical high temperature interdiffusion profile

Figure 8 :PbO profile perpendicular to the diffusion direction

(a) 1 100°C
(b) 1400°C

Figure 9 :Effective binary diffusion coefficient for PbO

Figure 10 :Predicted diffusion layer thickness versus temperature-time.

Figure 11 :Typical axial refractive index profiles (lens diameter 40 mm).

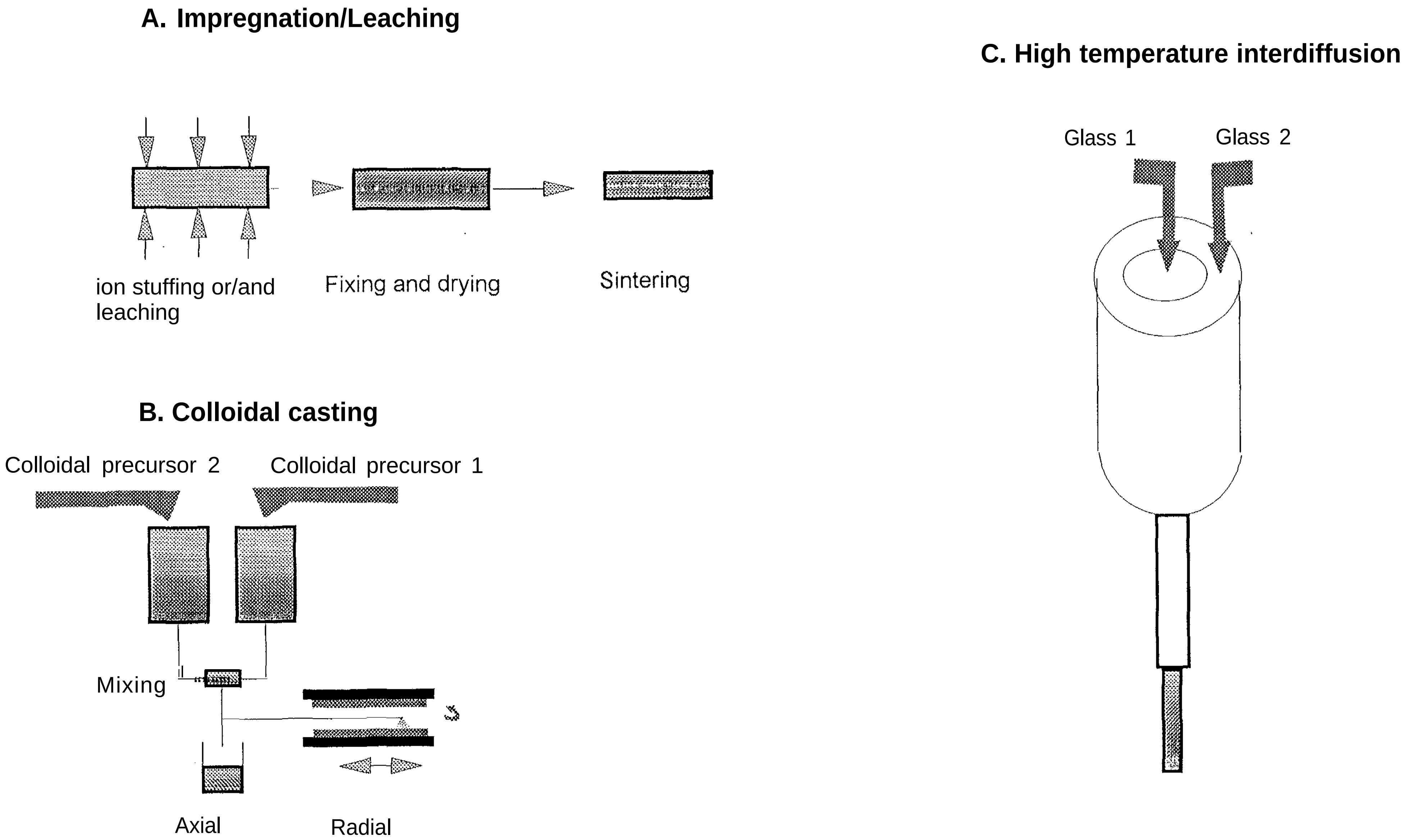
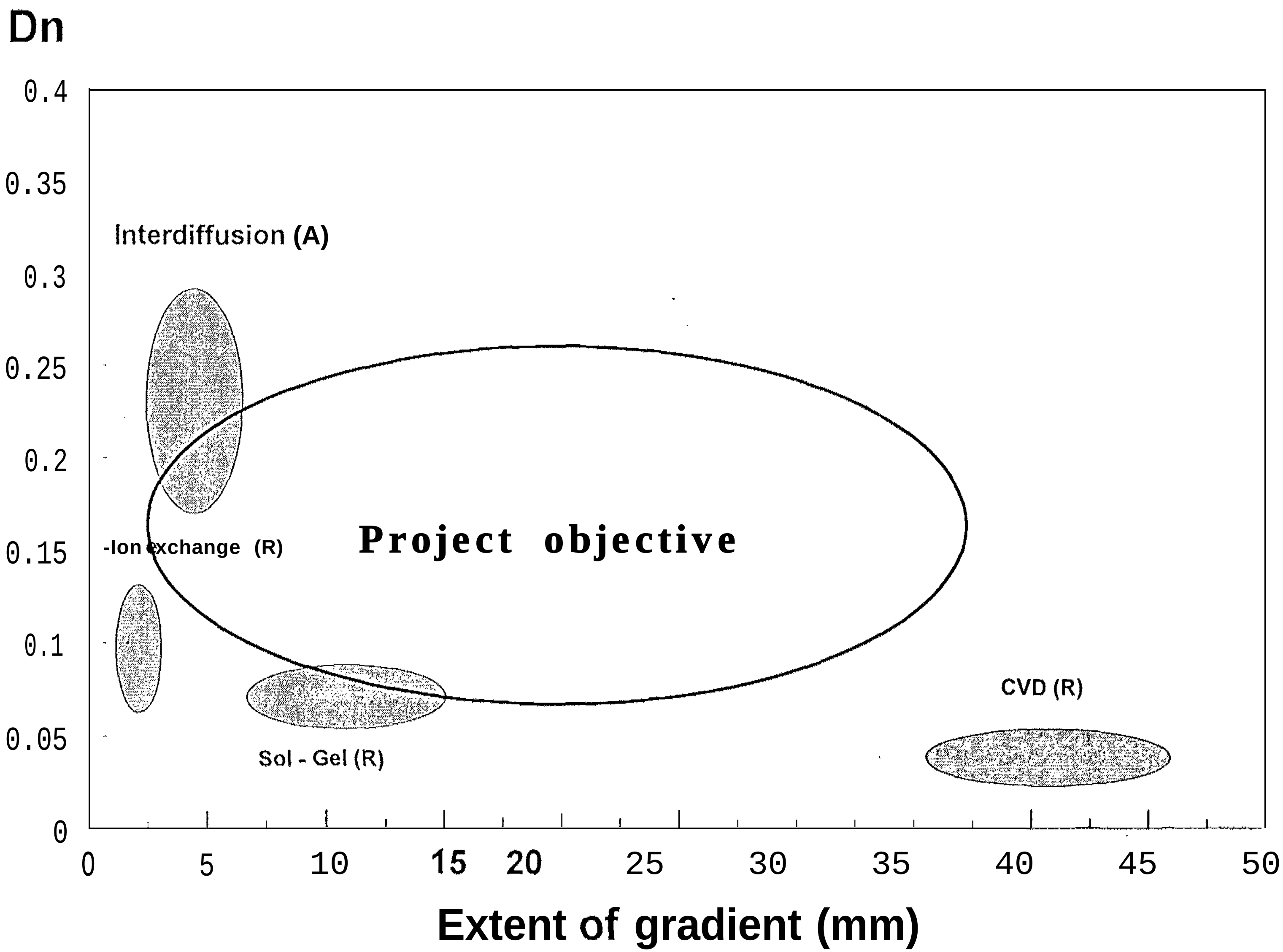

A. Impregnation/Leaching
ion stuffing or/and leaching
Fixing and drying
Sintering
B. Colloidal casting
Colloidal precursor 2
Colloidal precursor 1
Mixing
Axial
Radial
C. High temperature interdiffusion
Glass 1
Glass 2

fig. 1


Dn
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Interdiffusion (A)
-Ion exchange (R)
Project objective
Sol - Gel (R)
CVD (R)
0
5
10
15
20
25
30
35
40
45
50
Extent of gradient (mm)

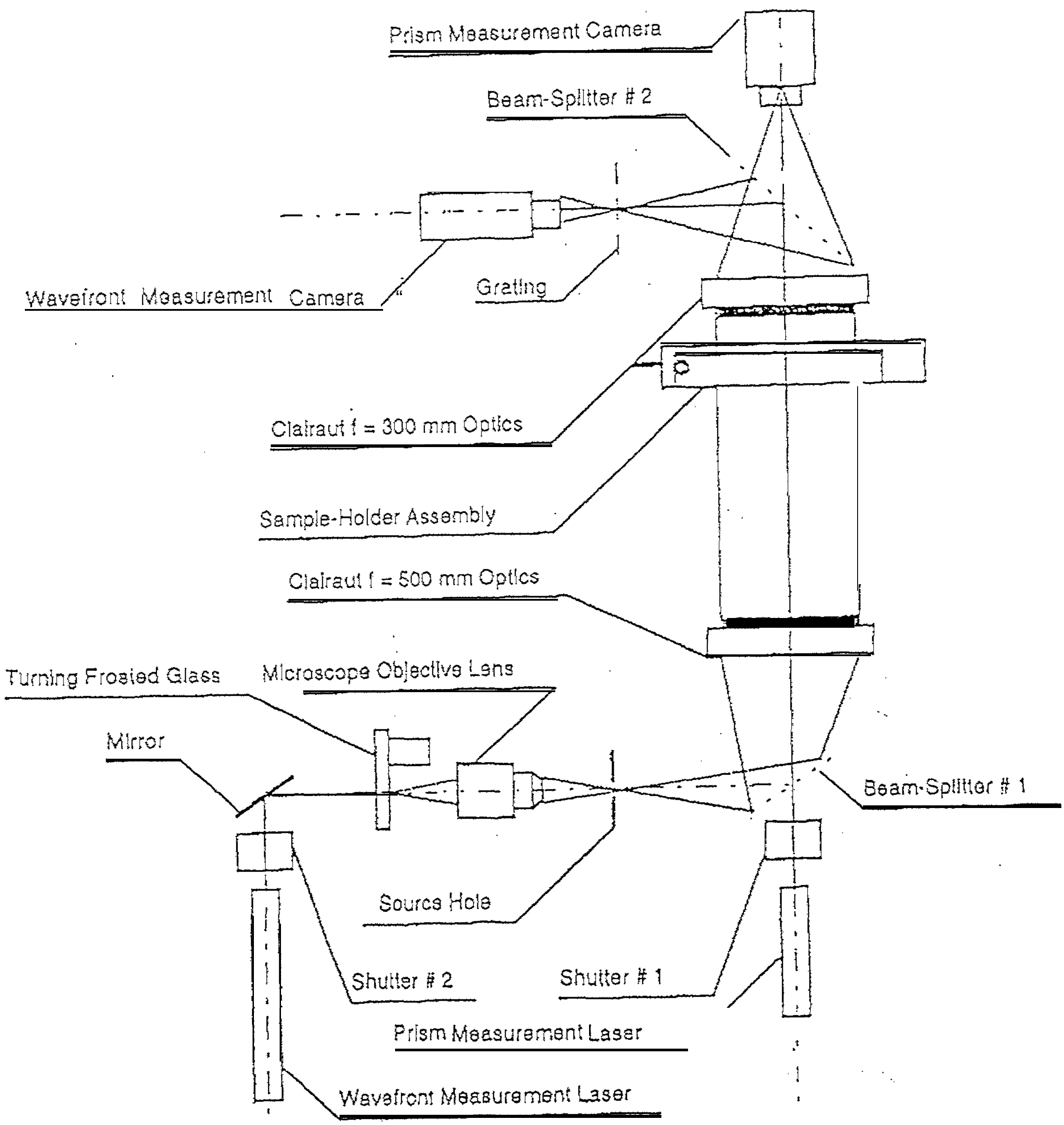

Prism Measurement Camera
Beam-Splitter # 2
Wavefront Measurement Camera
Grating
Clairaut f = 300 mm Optics
Sample-Holder Assembly
Clairaut f = 500 mm Optics
Turning Frosted Glass
Microscope Objective Lens
Mirror
Beam-Splitter # 1
Source Hole
Shutter # 2
Shutter # 1
Prism Measurement Laser
Wavefront Measurement Laser

fig. 3

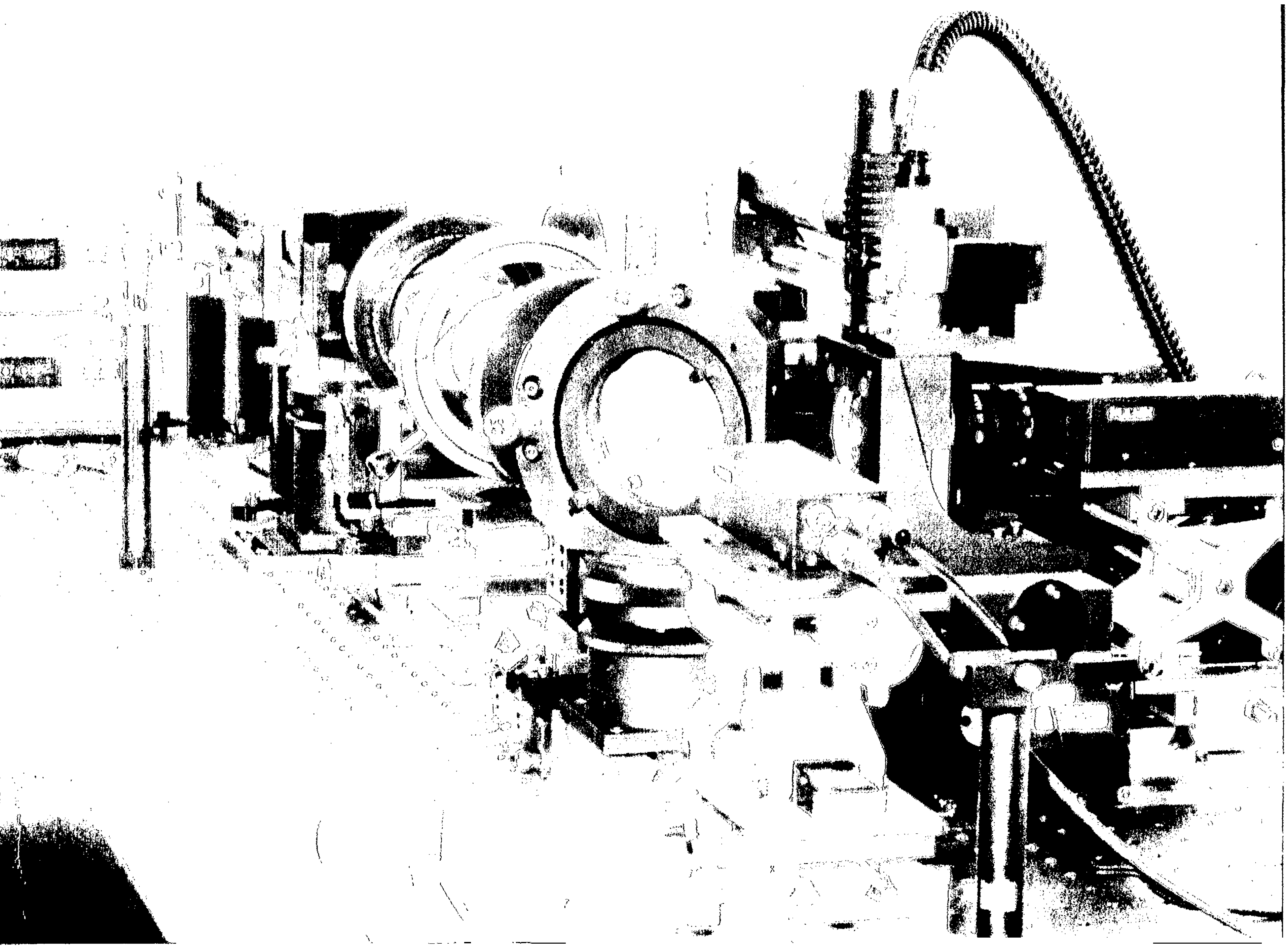
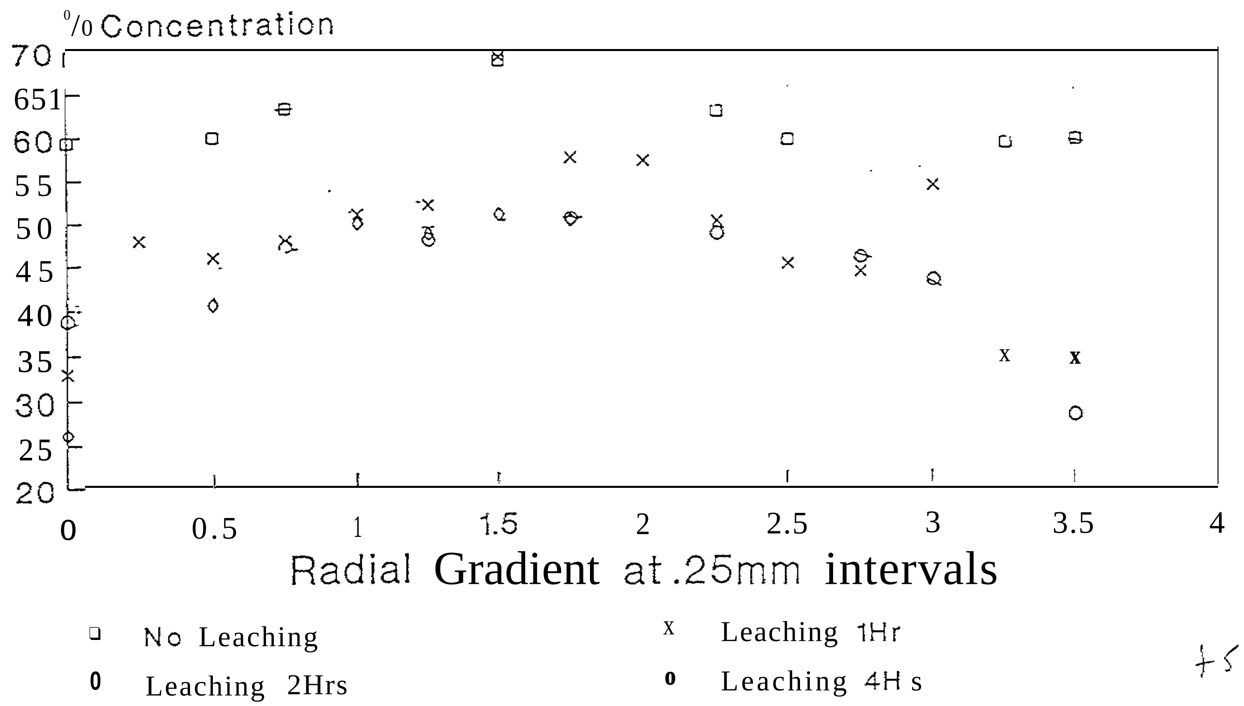
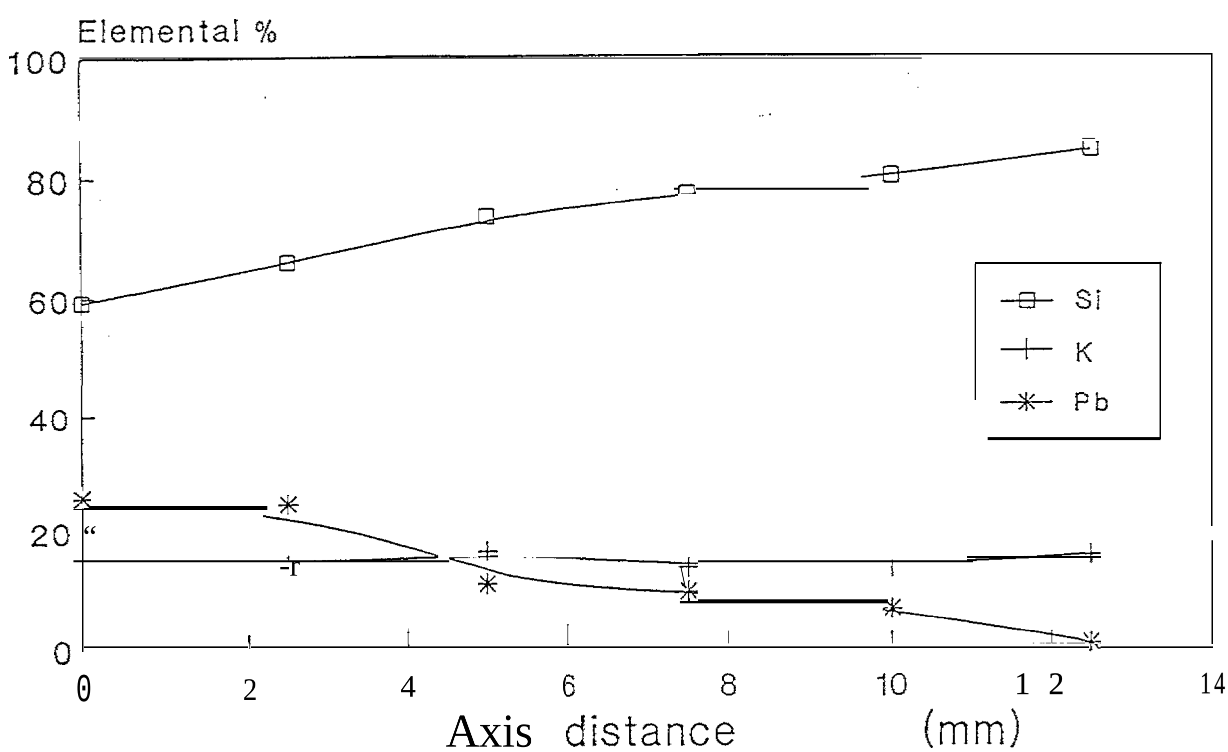


fig. 4



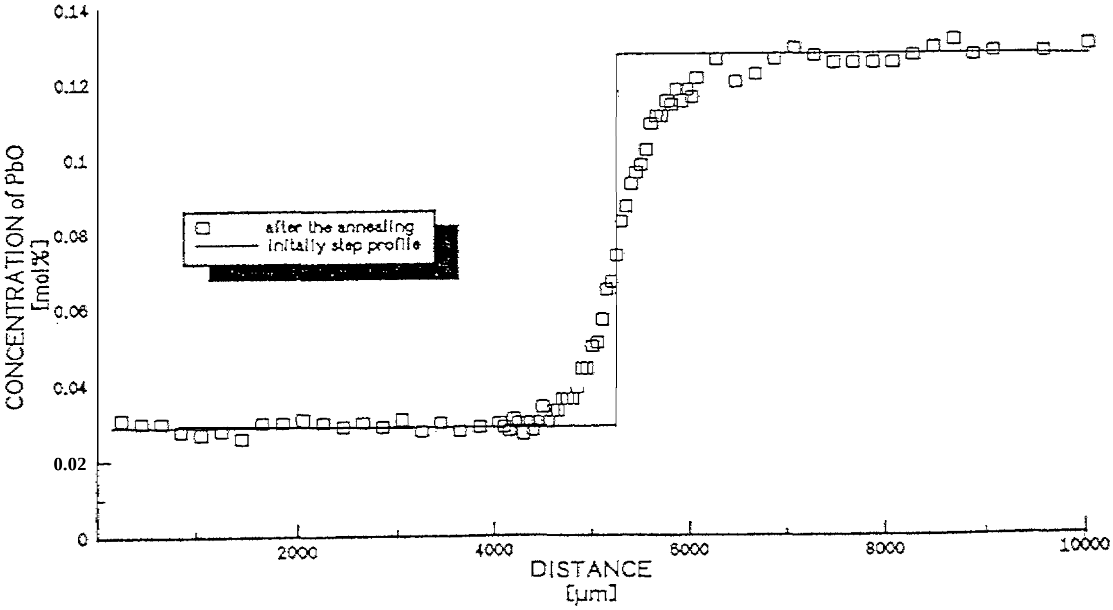
% Concentration
70
65
60
55
50
45
40
35
30
25
20
0
0.5
1
1.5
2
2.5
3
3.5
4
Radial Gradient at .25mm intervals
No Leaching
Leaching 1Hr
Leaching 2Hrs
Leaching 4Hrs

f5



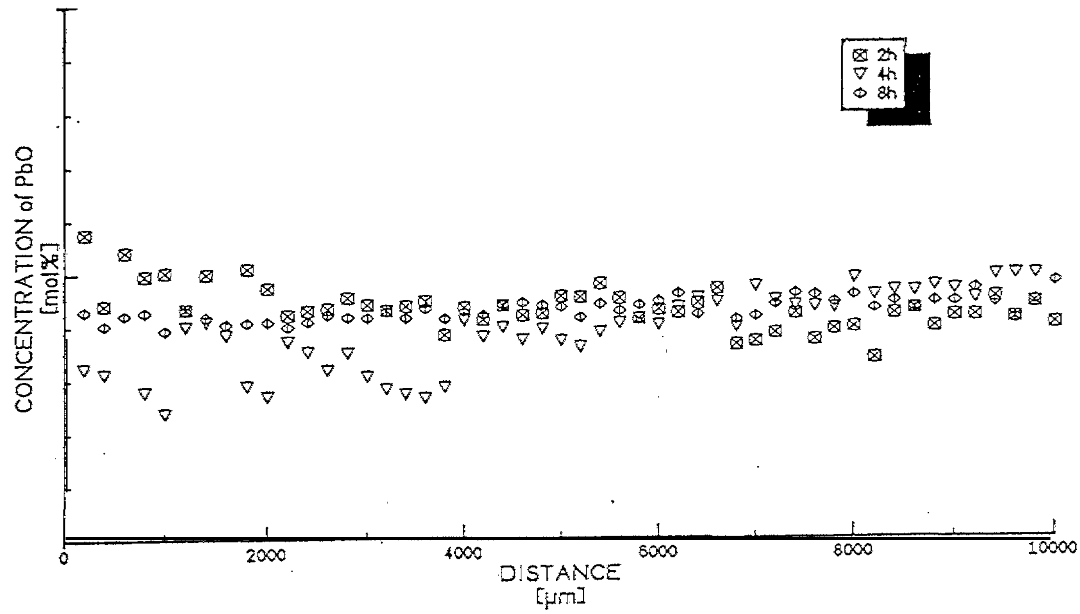
Elemental %
100
80
60
40
20
0
0
2
4
6
8
10
12
14
Axis distance (mm)
Si
K
Pb

f6



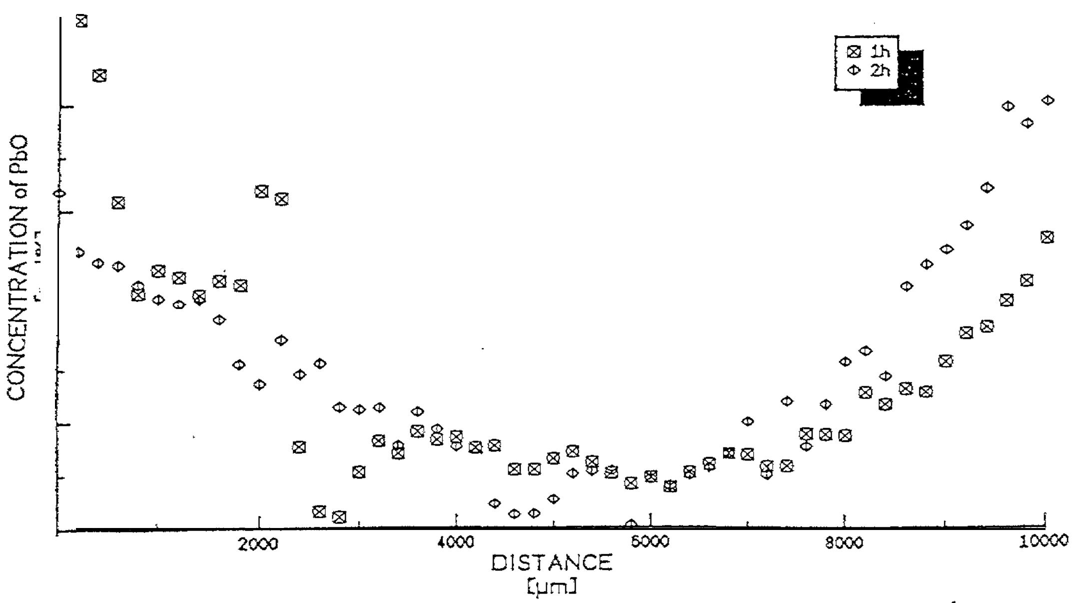
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
CONCENTRATION of PbO
[mol%]
after the annealing
initially step profile
2000
4000
6000
8000
10000
DISTANCE
[μm]

(a)



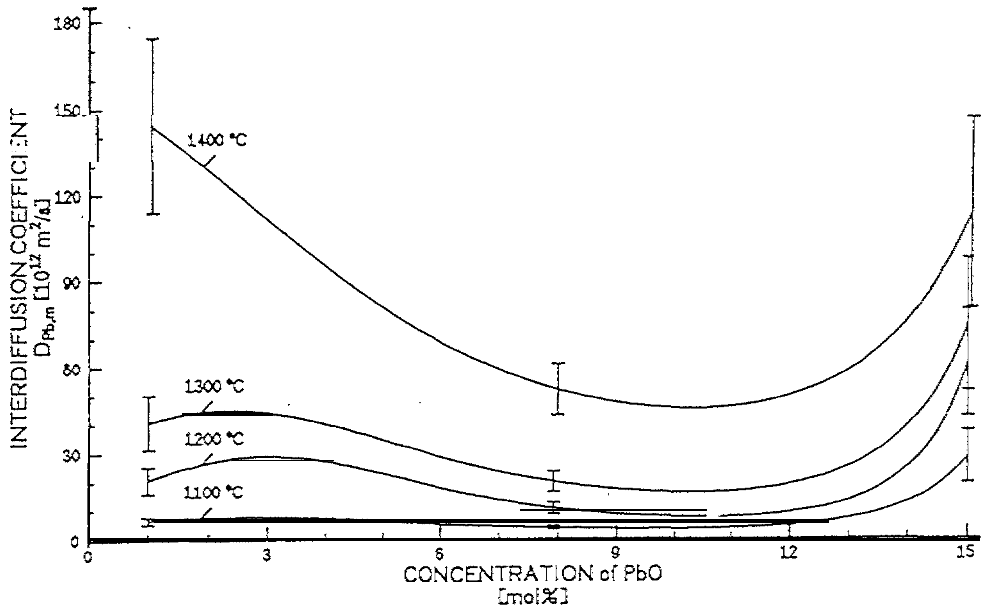
2h
4h
8h
CONCENTRATION of PbO
[mol%]
0
2000
4000
6000
8000
10000
DISTANCE
[μm]

(b)

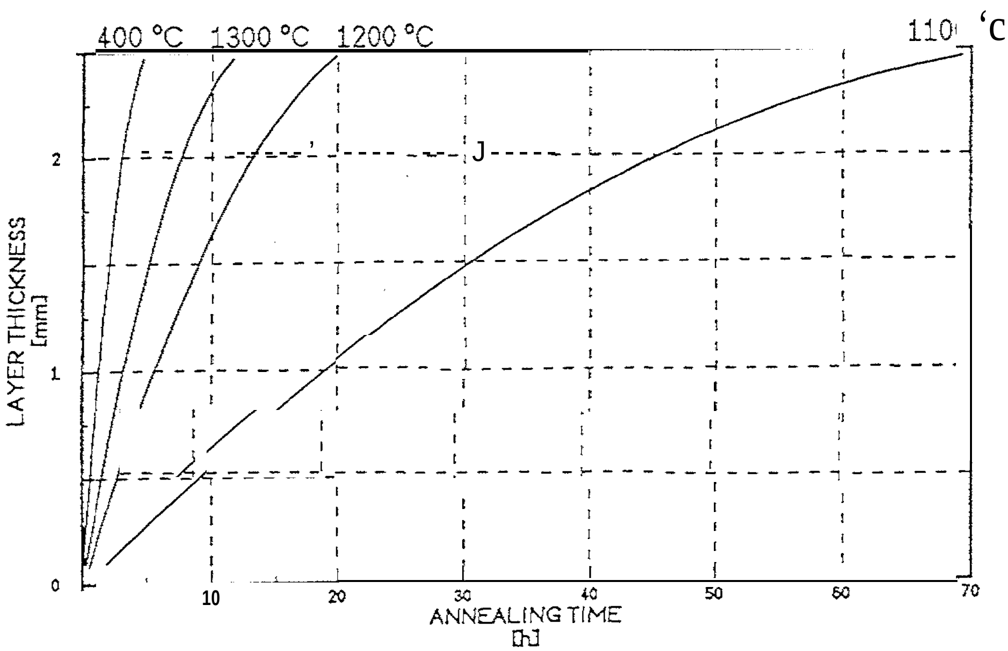


1h
2h
CONCENTRATION of PbO
2000
4000
6000
8000
10000
DISTANCE
[μm]

f 8


INTERDIFFUSION COEFFICIENT
$D_{Pb,m}$ [10^{12} m²/s]
1400 °C
1300 °C
1200 °C
1100 °C
CONCENTRATION of PbO
[mol%]

f9


400 °C
1300 °C
1200 °C
110 °C
LAYER THICKNESS
[mm]
ANNEALING TIME
[h]

f10

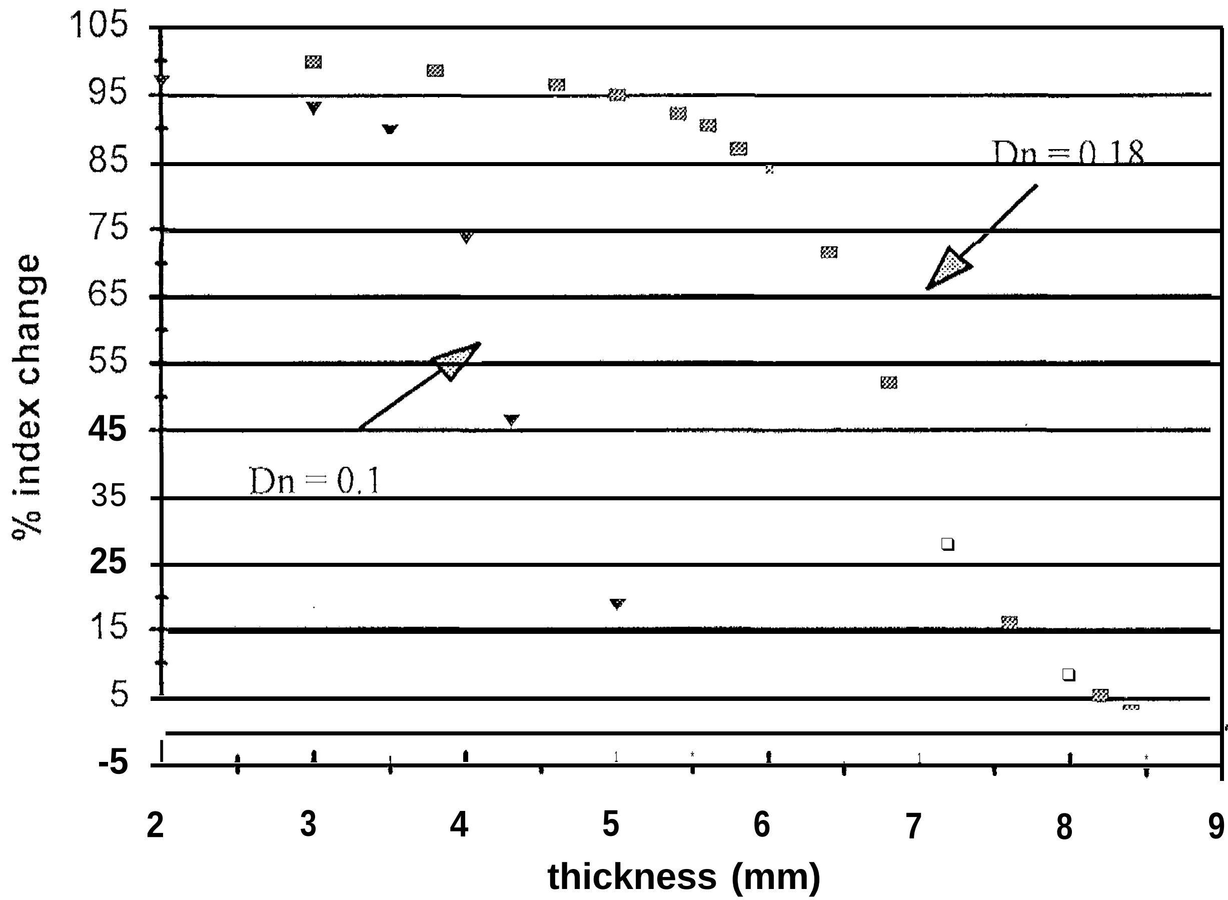

105
95
85
75
65
55
45
35
25
15
5
-5
% index change
Dn = 0.18
Dn = 0.1
2
3
4
5
6
7
8
9
thickness (mm)

Table I : Comparison of maximal thickness of axial GRIN lenses and homogeneous spherical and aspheric lenses with nearly identical optical properties (positive lenses).

Pius-Lenses $S'_{\infty} = +4D$

Type of glass	Index	Surface Power of front surface [dpt]	maximal Thickness [mm]	max. Index used in lens
inhomogeneous spherical	1.7- 1.6	5.0	4.1	1.666
inhomogeneous spherical	1.7- 1.5	5.0	4.6	1.580
inhomogeneous aspheric	1.7- 1.6	5.0	3.9	1.698
inhomogeneous aspheric	17-1.5	5.0	3.9	1.697
homogeneous aspheric	1.7	5.0	3.9	
homogeneous aspheric	1.666	5.0	4.1	
homogeneous aspheric	1.6	5.0	4.4	
homogeneous aspheric	1.580	5.0	4.5	
homogeneous aspheric	1.5	5.0	5.0	
homogeneous spherical	1.7	8.0	4.3	
homogeneous spherical	1.666	8.0	4.5	
homogeneous spherical	1.6	8.0	4.8	
homogeneous spherical	1.580	8.0	5.0	
homogeneous spherical	1.5	8.0	5.7	

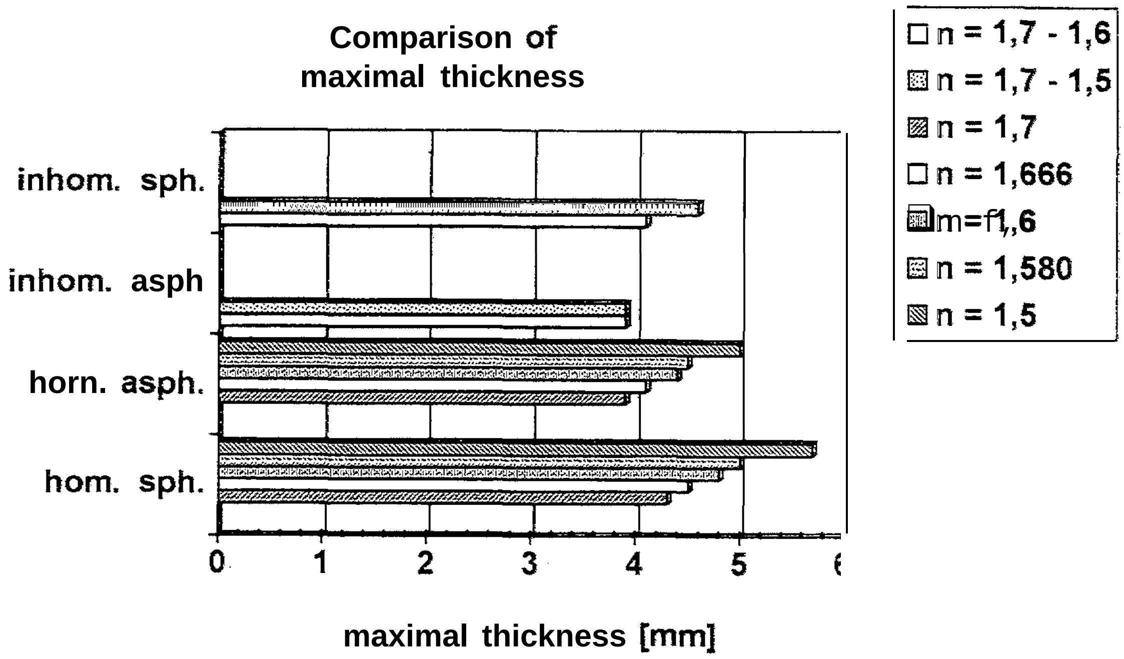


Table II : Comparison of maximal thickness of axial GRIN lenses and homogeneous spherical and aspheric lenses with nearly identical optical properties (negative lenses)

Mires-Lenses. $S'_{\infty} = -4D$

Type of glass	Index	Surface Power of front surface [dpt]	maximal Thickness [mm]	max. Index used in lens
inhomogeneous spherical	1.7- 1,6	2.0	4.5	1.671
inhomogeneous spherical	1.7- 1.5	2.0	5.4	1.544
inhomogeneous aspheric	1.7- 1.6	2.0	3.9	1.7
inhomogeneous aspheric	1.7- 1.5	2.0	3.8	1.7
homogeneous aspheric	1.7	2.0	4.0	
homogeneous aspheric	1.6	2.0	4.6	
homogeneous aspheric	1.5	2.0	5.4	
homogeneous spherical	1.7	3.5	4.4	
homogeneous spherical	1.6	3,5	5.0	
homogeneous spherical	1.5	3.5	5.9	

Comparison of maximal thickness