REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		FINAL 01 Jul 93 To 30 Jun 96

4. TITLE AND SUBTITLE
GRADIENT INDEX LENSES FROM SOL-GEL LAYERING

5. FUNDING NUMBERS
F49620-93-1-0364
3484/XS
61103D

6. AUTHOR(S)
Dr John D. Mackenzie

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California, Los Angeles
Dept of Materials Science & Engineering
405 Hilgard Avenue
6531 Boelter Hall
Los Angeles CA 90095-1595

AFOSR-TR-96
0491

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
110 DUNCAN AVE SUITE B115
BOLLING AFB DC 20332-0001

19961017 134

Approved for public release;
distribution unlimited

This is the third and final annual technical report of an AASERT grant award covering the period from 1 July 1993 to 30 June 1996. The research proposed is based on the concept of the liquid gradient density column,1 which is used to measure the density of doped semiconductors. This technique uses a column made from two miscible liquids of different densities, configured to exhibit a continuous variation in density from the bottom to the top of the column. With the most dense liquid at the bottom and the lighter liquid at the top, the gradient is a function of the starting densities of the starting materials. Such gradient columns are stable up to several months and allow an accuracy in density measurement of up to five significant digits. It is assumed that density differences can be directly correlated with differences in refractive index. In this research the principle of the gradient density column is applied to the sol-gel process. The sol-gel process has been widely studied in the recent past, as it is an interesting alternative chemical route to conventional glass and ceramics processing.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
(U)	(U)	(U)	(U)

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 1

Standard Form 298 (Rev. 2-89)

BEST AVAILABLE COPY

FINAL ANNUAL TECHNICAL REPORT

to

Air Force Office of Scientific Research

for project entitled

GRADIENT INDEX LENSES FROM SOL-GEL LAYERING
(An AASERT Award)

Grant No.: AFOSR-F49620-93-1-0364

Inclusive Dates: 1 July 1993 to 31 June 1996

PRINCIPAL INVESTIGATOR

John D. Mackenzie, Professor
Department of Materials Science and Engineering
Phone: (310) 825-3539
FAX: (310) 206-7353

Introduction and Background

This is the third and final annual technical report of an AASERT grant award covering the period from 1 July 1993 to 30 June 1996.

The research proposed is based on the concept of the liquid gradient density column,[1] which is used to measure the density of doped semiconductors. This technique uses a column made from two miscible liquids of different densities, configured to exhibit a continuous variation in density from the bottom to the top of the column. With the most dense liquid at the bottom and the lighter liquid at the top, the gradient is a function of the starting densities of the starting materials. Such gradient columns are stable up to several months and allow an accuracy in density measurement of up to five significant digits. It is assumed that density differences can be directly correlated with differences in refractive index. In this research the principle of the gradient density column is applied to the sol-gel process. The sol-gel process has been widely studied in the recent past, as it is an interesting alternative chemical route to conventional glass and ceramics processing. The set-up is simple and is illustrated in Figure 1. Two sols having difference in density are placed in two separate containers. the beakers are positioned in such a way as to allow the lower density liquid to be fed into the higher density liquid, at a controlled rate with stirring. As soon as the higher density liquid (in container 2) is allowed to flow into the higher density liquid. In this manner, the density of liquiid 2 is gradually altered and a gradient in density is formed as the liquid of changing composition and density and hence changing refractive index, is fed into an empty container. The gradient index liquid column is then allowed to gel. The solid gel column is then densified to become a glass with gradient index. Currently, there is a fairly widespread interest in gradient refractive index (GRIN) lenses. The most important applications include photocopier,[2] medical endoscopes,[3] video

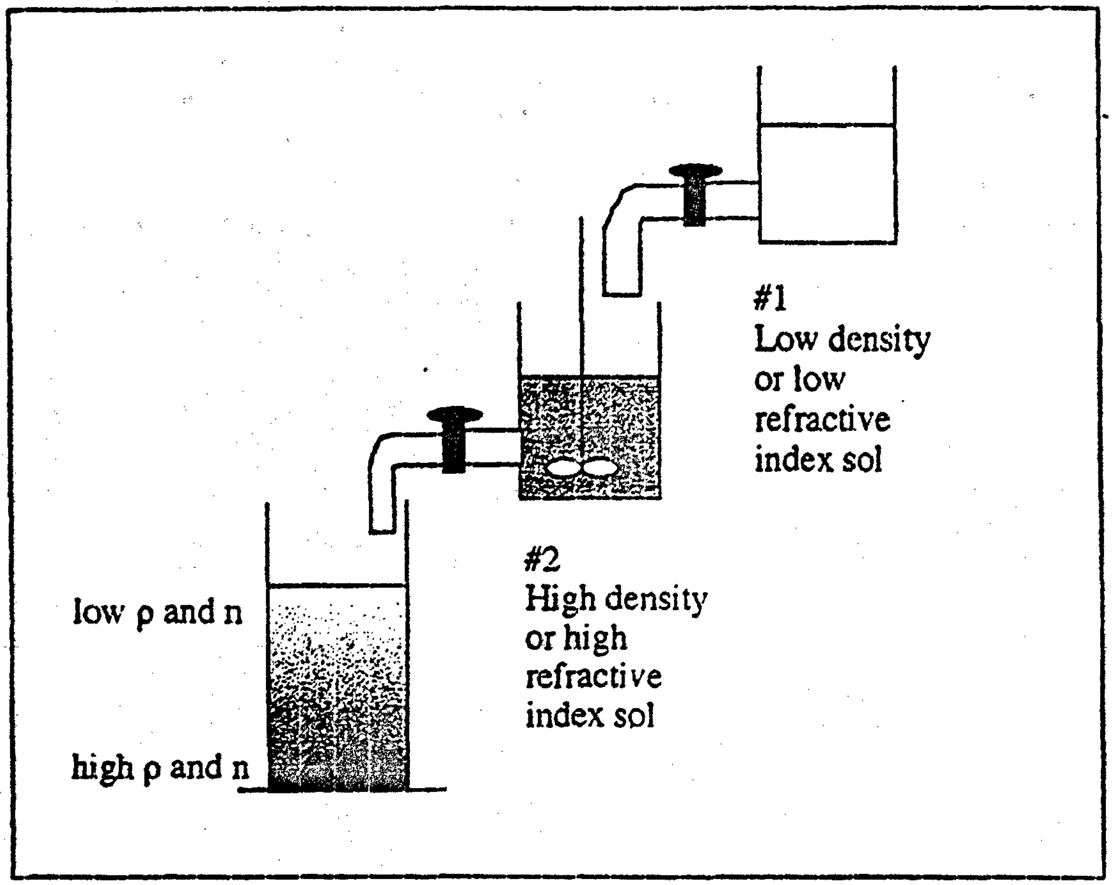


Figure 1. A schematic drawing of the gradient casting set-up.

or compact disc systems,[4,5] and a wide variety of devices for optical fiber communications.[6] At present, several techniques are used to produce gradient index glass[7-10] but most of the processes are limited by the small index change they are able to achieve, as well as the small size of the gradient region. The present method is new and unique. The successful preparation of dense GRIN lenses by the UCLA technique should find immediate applications.

The first system chosen for a demonstration of this technique for the fabrication of an axial gradient refractive index glass was SiO_2-TiO_2. It is well known that the addition of titania to silica leads to an increase in refractive index. Furthermore, this system has been extensively studied. It was expected that by feeding a SiO_2 sol into an SiO_2-TiO_2 sol, a gradient in composition can be formed and hence a gradient in refractive index can be obtained. Other systems selected for demonstration were the PbO-TiO_2 and ZrO_2-TiO_2 systems since high refractive index glasses have already been prepared by the sol-gel method.

2. Research performed

(a) The TiO_2-SiO_2 System

TiO_2-SiO_2 and SiO_2 sols were prepared following the procedure outlined in Figure 2. Tetramethylorthosilicate (TMOS, 98% purity) and titanium isopropoxide (TiOP, 97% purity) were purchased from Aldrich Chemical Company. Metehanol, 99.8% pure, and hydrochloric acid 37%, were both obtained from Fisher scientific.

Because of differences in gelation times between SiO_2 sols and TiO_2-SiO_2 sols, as the Ti/Si ratio changes, it was necessary to adjust the chemical composition of the SiO_2 sol. For higher titanium in the system, a lower acid content was required. Three compositions in the TiO_2-SiO_2 system, containing

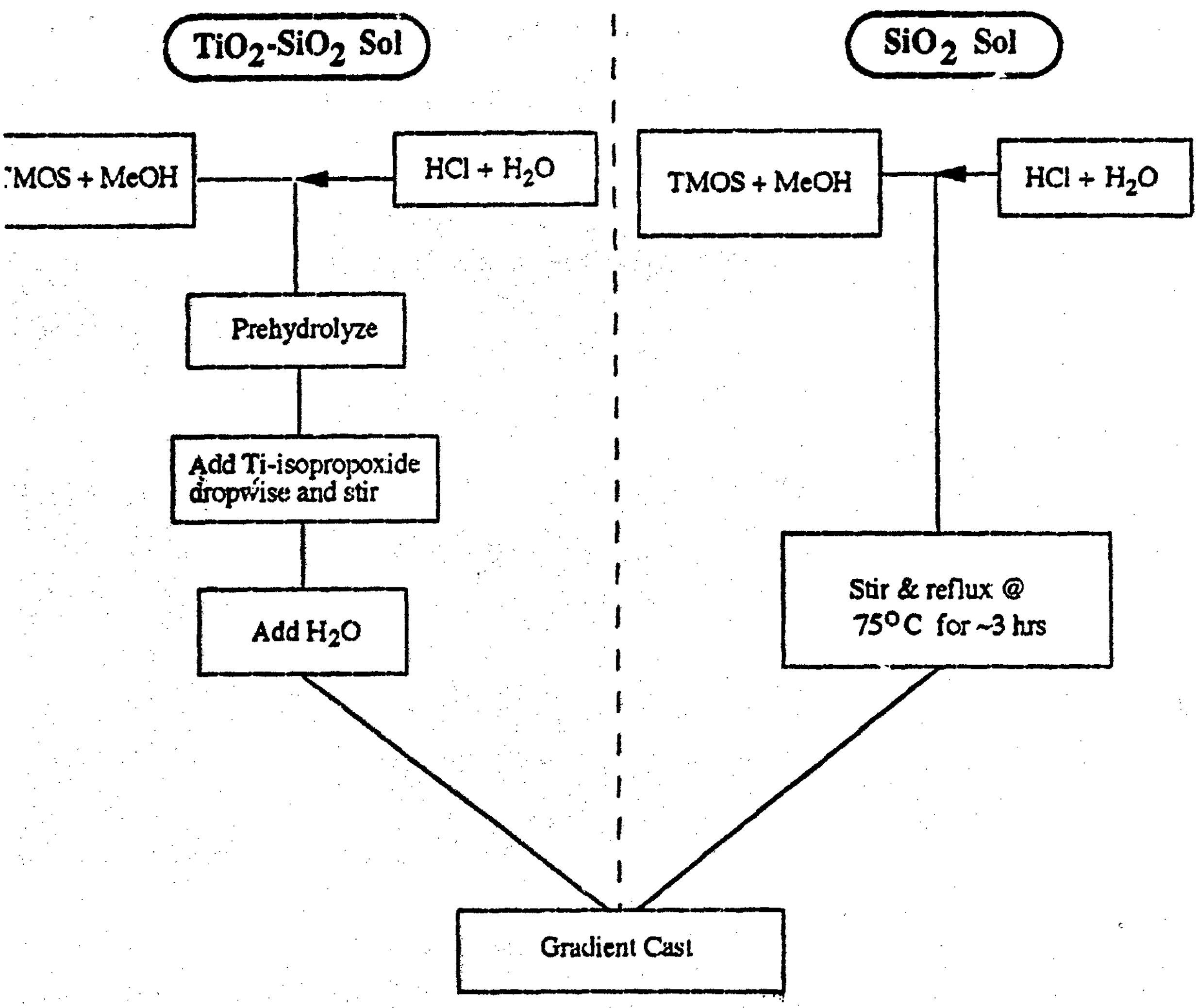


Figure 2. Flow chart illustrating the preparation steps of the TiO_2-SiO_2 and SiO_2 sols.

7.5, 15 and 30 mol% Ti were studied. All chemical compositions are listed in Table 1.

The SiO_2-TiO_2 solutions were prepared via prehydrolysis of the TMOS. The silicon alkoxide was prehydrolyzed with one mole of water per mole of TMOS, prior to the addition of the remaining alkoxide/alcohol/water solutions.

As far as the pure SiO_2 sol is concerned, it was prepared according to the compositions listed in Table 1, and then refluxed for 3 hours in order to bring the gelation time to close to that of the TiO_2-SiO_2 sols.

Following the sol preparation, the sols were cast according to the set-up described earlier and represented in Figure 1. Equal volumes (25 ml) of TiO_2-SiO_2 and SiO_2 sols were placed into two separate glass beakers equipped with a faucet. Because the TiO_2-SiO_2 sol had a higher density than the SiO_2 sol, it was placed in beaker number 2. The flow rate of the SiO_2 sol pouring into the TiO_2-SiO_2 sol was adjusted to twice that of the TiO_2-SiO_2 sol being fed into the empty polypropylene container. Therefore, both beakers numbers 1 and 2 emptied simultaneously.

After gradient casting, the containers were tightly sealed and placed in an oven at 50°C. Gelation took place within a few hours. The GRIN gels were aged for one day and allowed to dry for 1 week at 50°C. Pinholes were made in the cover seals and the gels were dried at 120°C. some of the gels were further heat-treated up to the desired temperature at a slow ramp rate (0.5 - 1°C/min).

Energy dispersive X-ray analysis (EDX) (Kevex Inst.) was performed on a Scanning Electron Microscope (Cambridge/Stereoscan 250). Analysis was carried out on along the gradient axis of both dried and fired gels. Refractive index measurements were carried out on cut segments of a GRIN glass using the Becke Line method. The gel segments were obtained by cutting partially-

Table 1 - Chemical Composition of Gels

Sol	Alkoxides	iPrOH	H_2O	HCl
$7.5TiO_2$-$92.5SiO_2$	1	5	10	0.1
SiO_2 Sol	1	5	10	0.05
$12TiO_2$-$88SiO_2$	1	3	4	0.05
SiO_2 Sol	1	3	7	0.1
$30TiO_2$-$70SiO_2$	1	2	2.6	0.005
SiO_2 Sol	1	3	4	0.15

dried gels perpendicular to the gradient axis. The segments were subsequently heat-treated to 900°C. Gels were immersed in liquids of known refractive indices, purchased from Cargille Laboratories. The existence of a gradient was visually demonstrated by bending a He-Ne laser light beam through GRIN gels. The EDX results for a dried and a fired GRIN gel are shown in Figures 3 and 4. Both plots show a gradient in composition. for the dried $30TiO_2$-$70SiO_2$ gel, some titanium is present at the bottom of the sample, as 10% Ti is the minimum Ti concentration achieved. A similar feature is observed for a fired gel (Figure 4). It is apparent that profiles are retained from the solution through the dried stagers. Some deviation from a straight line gradient are observed, is ascribed to slight deviations from ideal flow rates.

The attainment of composition gradient is confirmed by refractive index measurements as shown in Figure 5 for a 15 TiO_2-$85SiO_2$ GRIN. A refractive index difference $\Delta n = 0.07$ is achieved for a sample size of 10 mm. The silica-rich end of the GRIN had a refractive index of 1.474 at a distance of 1 mm away from the tip; whereas the titania-rich side of the sample exhibited a refractive index of 1.544. If the relative flow rates were slightly modified, a different profile resulted, as shown in Figure 6. A GRIN sample made from identical starting solutions was made, and the flow rate of the TiO_2-SiO_2 sol was adjusted to a slightly higher value. The resulting gradient profile is slightly different with Δn of 0.04.

Previous work on the SiO_2-TiO_2 gel systems have shown that up to 25 wt.% of TiO_2 could be added to SiO_2. leading to increases in refractive index and density. Hench showed that a simple containing 3% TiO_2 had a refractive [illegible] refractive index and its correlation with chemical composition in the gradient are in reasonable agreement with our work.

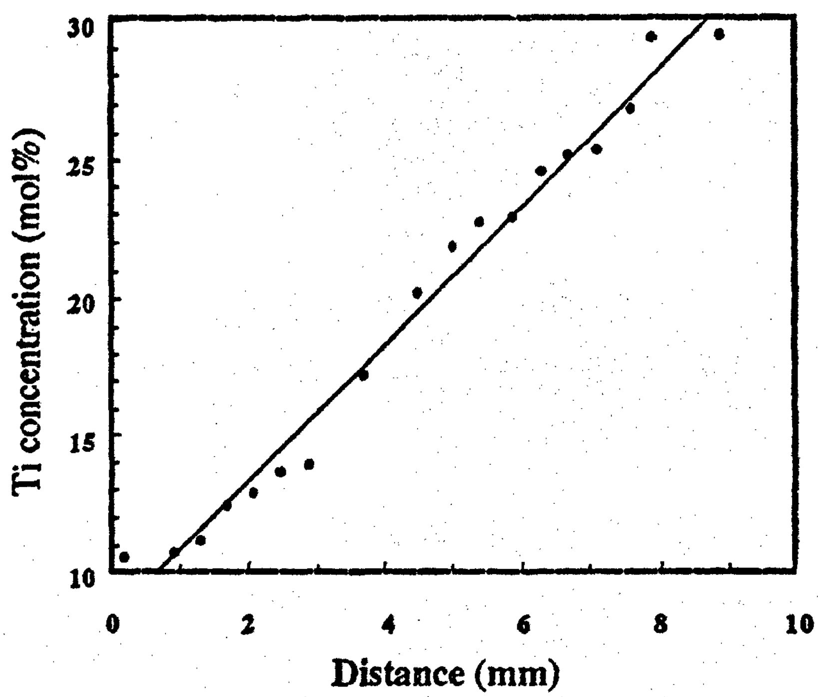


Figure 3. Plot of the Ti concentration vs. distance for a $30TiO_2$-$70SiO_2$ GRIN gel dried at 120°C.

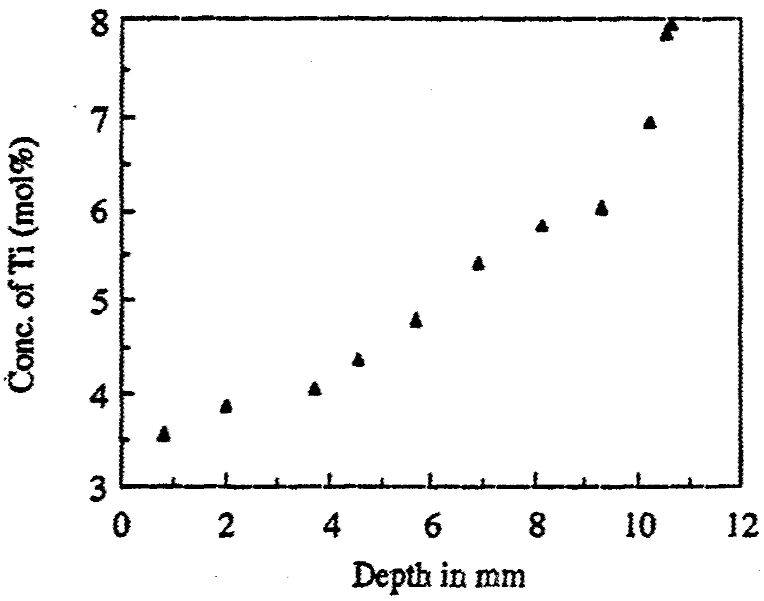


Figure 4. Plot of the relative Ti concentration vs. depth in mm for a $7.5TiO_2$-$92.5SiO_2$ GRIN gel fired to 600°C.

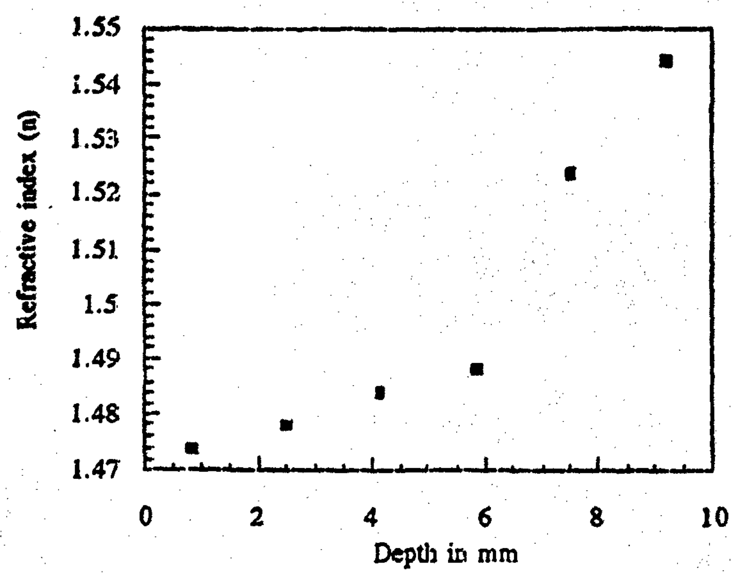


Figure 5. Refractive index as a function of depth for a $15TiO_2$-$85SiO_2$ GRIN glass #1.

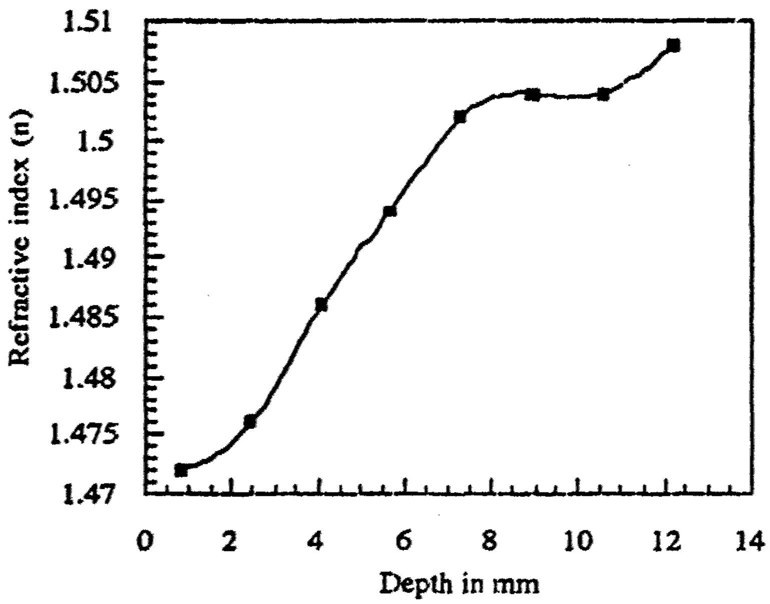


Figure 6. Refractive index as a function of depth for a $15TiO_2$-$85SiO_2$ GRIN glass #2.

A He-Ne laser light beam was used to demonstrate optically the presence of the gradient. In a wet gel. Figure 7 shows that the bending is present shortly after gelation. It is also visible after the gel has been dried (Figure 8). The beams are visible in both materials because of some scattering due to their porosity.

Although the TiO_2-SiO_2 system was selected for this experiment, it is clear that any other system could be used. Ternary systems, which would increase the maximum theoretical Δn, may also be considered. A key element in the success of the process is that the reactivity of both starting sols (.e., their gelation times) must be similar. A large disparity between gelation times leads to casting difficulties or inhomogeneities. If gelation times are not similar, they must be made so by appropriate chemical modifications of the alkoxides. Current research efforts are placed on the study of profile tailoring as well as densification of sol-gel derived GRIN glass.

(b) The SiO_2 - PbO System

TiO_2-PbO monoliths have recently been fabricated by the sol-gel technique.[11] Although these materials were initially investigated for their high nonlinear optical coefficients, they are of great relevance to our study because they also exhibit a large variation in refractive index with composition. Transparent glasses have been fabricated over a wide compositional range. The refractive index of a 60%mole TiO_2-40%mole PbO is 2.030, and that of a 805 TiO_2-20% PbO is 2.268. Two solution compositions were prepared, one containing 80T TiO_2 (solution A), the other 60% TiO_2 (solution B), were prepared. Using the set-up previously described, a gradient gel was cast in polypropylene containers. The refractive indices of gels of both extreme compositions are presented in Table 2. These values were obtained by ellipsometry on thin films (0.2 - 0.4 μm) deposited on silicon substrates by

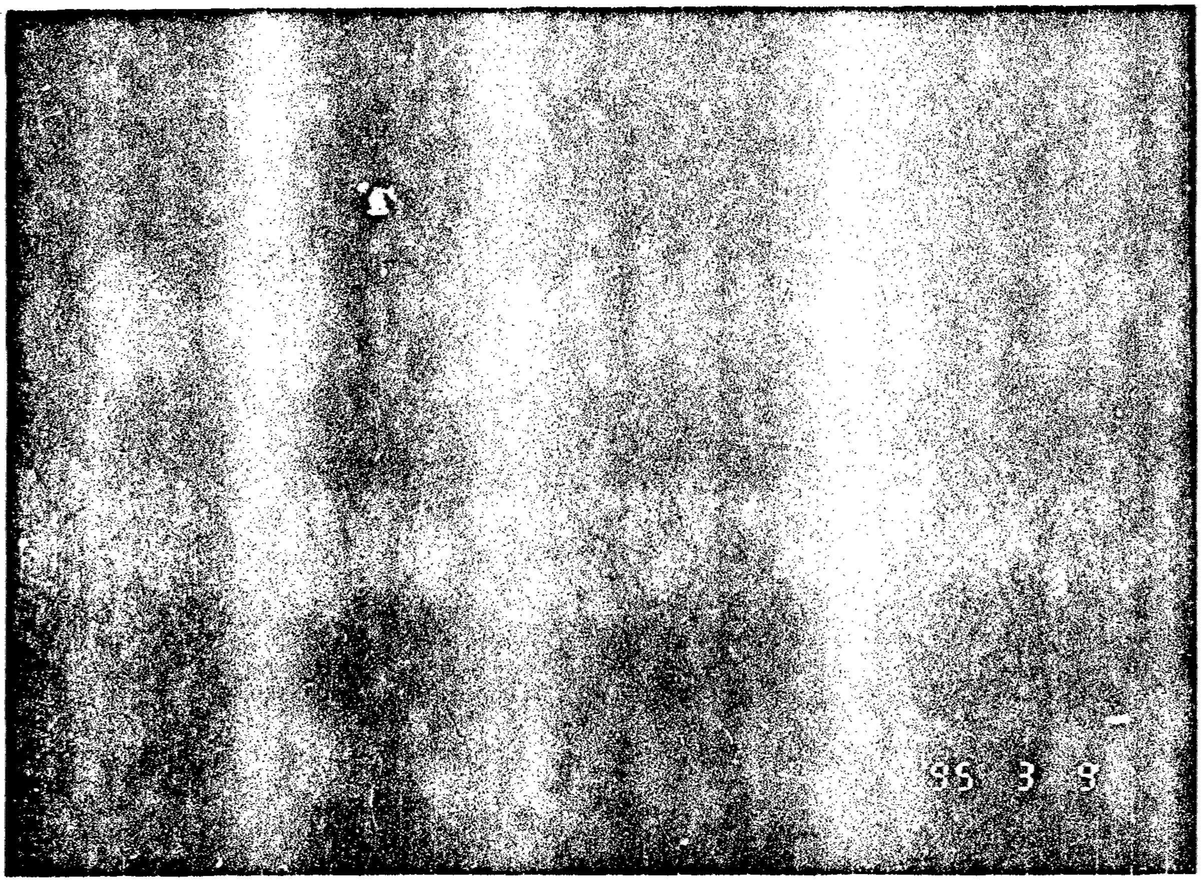


Figure 7 He-Ne light beam bending through a wet TiO_2-SiO_2 GRIN gel

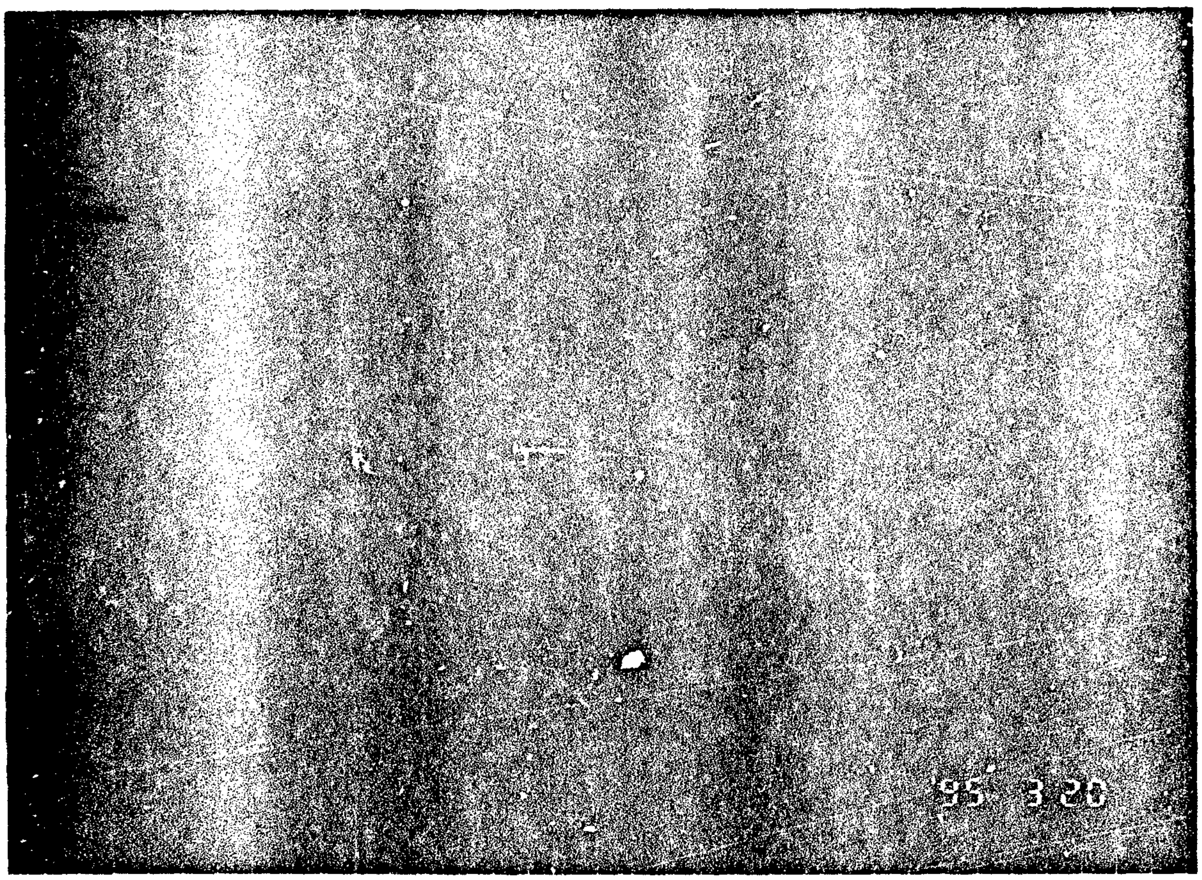


Figure 8 He-Ne light beam bending through a TiO_2-SiO_2 GRIN gel dried at 120°C

spin-coating. The maximum Δn measured was 0.38 for a gel dried at room temperature and 0.28 for a gel fired at 500°C for 1/2 hour.

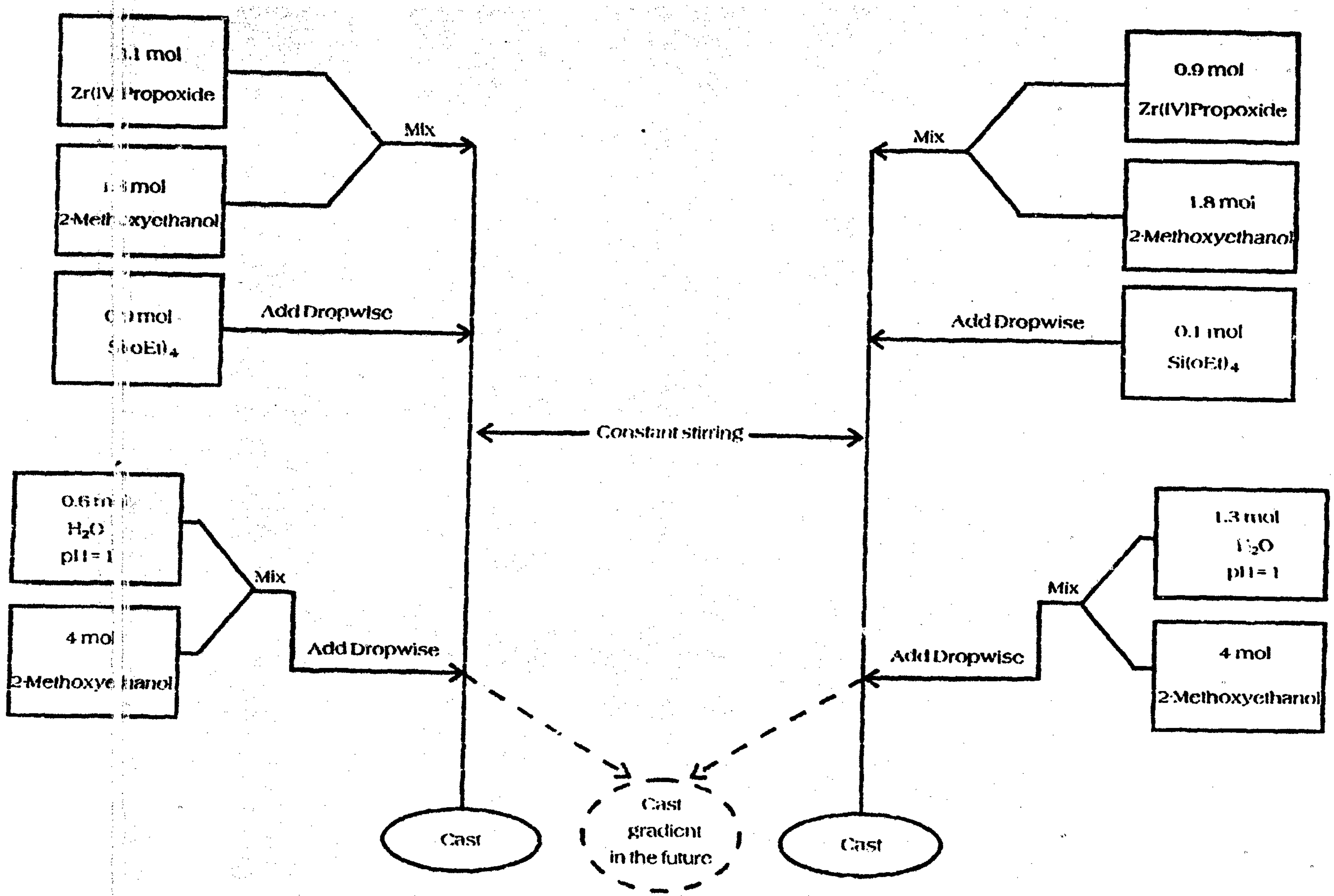
Table 2 - Refractive Indices of PbO-TiO_2 Gels

	$80TiO_2$-$20PbO$	$60TiO_2$-$40PbO$	Δn
n_D (gel	1.77	2.15	0.38
n_D (500°C)	2.84	2.56	0.28

The Δn value of the fired gels are in agreement with that reported by Nasu et al.[11] The existence of an axial gradient was demonstrated by observing the path of a laser beam though a wet gel.

(c) The ZrO_2 - SiO_2 System

ZrO_2-SiO_2 gels with ZrO_2 contents ranging from 10 mol% to 90 mol% were prepared according to the procedures shown in Figure 9 with the use of 2-methoxyethanol as the solvent. This was found to be superior to ethanol. The solvent/water ratios had to be altered for each composition to avoid precipitation and to enable the formation of clear gels. Samples of ZrO_2-SiO_2 gels are shown in Figure 10. Theoretically, if dense glasses can be made, large refractive index gradients can be achieved with this system since the refractive index of a 50 ZrO_2-50 SiO_2 glass is reported to be 1.865,[12] and that of a 90% ZrO_2 sample should approach 2.3.



Figur 9 Flowchart illustrating preparation of 10%ZrO_2- 90%SiO_2 and 90%ZrO_2 - 10%SiO_2 sols (in mol%)

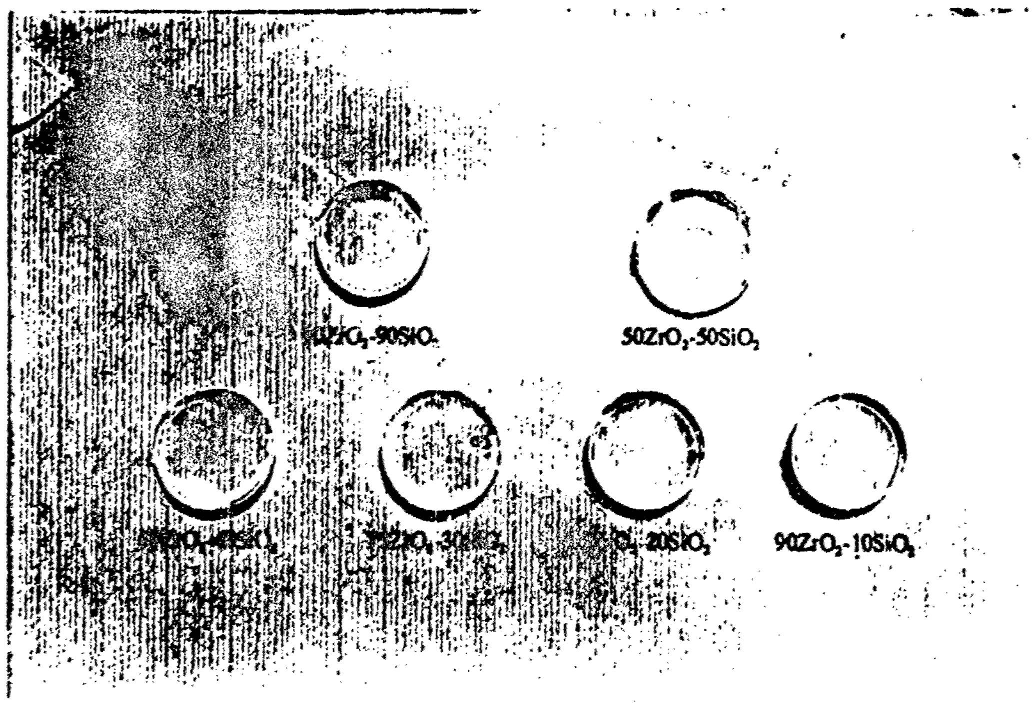


Figure 10 Transparent ZrO_2-SiO_2 gels prepared by the use of 2-methoxyethanol as solvent

(d) Preparation of Dense Glass Gradient Samples

In order to fabricate a dense glass sample from the gel, the latter must be first dried, washed to remove unreacted organics and then heated to some temperatures for the oxidation of all the trapped remaining organics prior to densification. During the last year of this program, we have succeeded in the removal of all the remaining trapped organics to obtain small clear glass samples. However, the last problem was the brittle fracture of the glass during firing. Up to the conclusion of this project on 30 June 1996, we were unable to fabricate an entire unbroken gradient dense glass sample. Further research must carried out to optimize the firing procedures before a gradient dense glass lens can be made.

3. Student Training

Three female U.S. citizens have been trained under this AASERT grant. Ms. Eva Wong and Ms. Tammy Chau both received their M.S. degrees in Materials Science and Engineering and are employed by industry in California. A third graduate student, Ms. Willa Larsen is currently completing her M.S. thesis at UCLA under Professor J.D. Mackenzie.

4. References

1. F.H. Horn, Physical Review, **97** (1955) 1521.
2. M. Kawazu and Y. Ogura, Applied Optics, **19** (1980) 1105-1112.
3. D.C. Leiner Miniature Optics in the Hospital Operating Room" in: **Gradient-Index Optics and Miniature Optics**, SPIE, 935 (1988) 52.
4. D.T. Moore, "Spherical Gradient-Index Lens Designs for Video-Disk Pickup Lens or the Like," U.S. Patent 4,457,590. July 3, 1994.

5. P.O. McLaughlin, M. Toyama, I. Kitano, "Axial Gradient Index Singlet Collimator Lens for the Compact Disk System, **Optical Mass II**, SPIE, 695 (1986).

6. W.J. Tomlinson, "Applications of GRIN-Rod Lenses in Optical Fiber Communication Systems," Applied Optics, **19** (1980) 1127-1138.

7. I. Kitano, K. Koizumi, H. Matsumura, T. Uchida, and M. Furukawa, J. Japan Society Appl. Phys. Suppl. **39** (1970) 63.

8. S. Konishi, K. Shingyouchi and A. Makishima, J. of Non-Crystalline Solids, **100** (1988) 511.

9. M. Yamane, A. Yasumori, M. Iwasaki and K. Hayashi, "Graded Index Materials by the Sol-Gel Process," in: Sol-Gel Optics, SPIE, **1328** (1990) 133-144.

10. J.B. Caldwell and D.T. Moore, U.S. Patents 4,797,376, January 10, 1989.

11. H. Nasu, K. Kamiya, Y. Katagiri, S. Makino, J. Matsuoka, Sol-Gel Optics III. SPIE Proc. **2288** (1994) 435-444.

12. M. Nogami, J. Non-Crystalline Solids, **69** (1985) 415-423.