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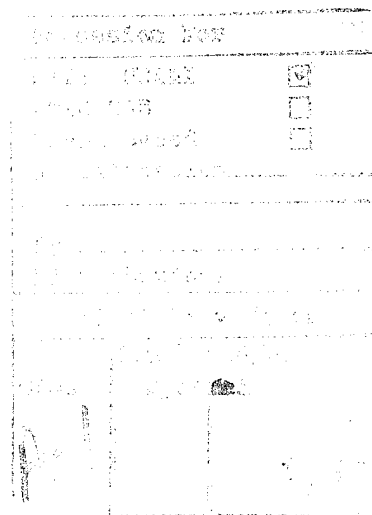
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**October 27, 1995**

# REFRACTIVE INDEX GRADIENT (GRIN) LENS VIA THE SOL-GEL PROCESS

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## 1. Introduction

Optical materials which contain a distributed refractive index and are used in lens design are called gradient-index (GRIN) materials which have wide applications in optical systems. The axial GRIN (AGRIN) has the iso-indicial surface in planes, and the index is a function of the coordinate along the optical axis only; the radial GRIN (RGRIN) has the iso-indicial surfaces about the optical axis, and the index is a function of the coordinate along the radial axis. These AGRIN lenses are particularly well suited for use in high-performance laser-based system because of their diffraction-limited focusing performance, high power-handling capability, and low surface scatter. Additionally, they eliminate the need for aberration-correcting optical elements, which means AGRIN lenses can reduce the size, weight, complexity, and cost of the optical systems. It is expected that the GRIN lens technology will stretch optical performance limits and simplify the design of optical systems which will meet the continued need to reduce cost and improve performance of future scientific payloads involving optics. Both types of GRIN materials are currently used for lens systems for compact copiers, compact audio/video discs, etc. and are expected to be applied in the near future to more complicated systems such as cameras, binoculars, microscopes and so on [1-4].

There are various approaches to fabricate GRIN materials. One of the methods is through the exchange of index-modifying ions in a glass with other ions in a molten salt bath [5]. Another approach is through the stuffing and partial unstuffing of a porous glass followed by subsequent drying and sintering [6]. A third method involves the formation of a porous precursor gel having a concentration gradient of index-modifying cations via the sol-gel process, and then densifying the gel into a solid radial GRIN glass through sintering [7]. Neutron irradiation [8], diffusion in plastics [9], chemical vapor deposition [10], and crystal growth [11] have been explored as techniques to make GRIN materials. However, these processes are limited by the small achievable index change, the small depth of the gradient region, the lack of control of the shape of the resultant index profile, and cost. Recently, a technique based on fusing together thin layers of glasses of progressively different indices of refraction was developed to produce gradient refractive indices in glass lens blanks of macro size;  $\Delta n$  values up to 0.5 have been achieved [12-15]. This technique presents a brand new concept of **layering engineering** to make GRIN materials with the design property profile. However, this technique is still dependent on the diffusion of the glass layers which is not fully controllable and is unable to make small precise high performance AGRIN samples for compact optical systems due to the use of thick glass plates or glass powder layers.

It is well known that glass can be prepared by the low-temperature sol-gel process. Various silica and silicate optical lenses have been fabricated via this process. The sol-gel process has also been utilized to make the radial GRIN lenses by the diffusion of the index-modified cations. Since the sol-gel process starts with solutions, layering is expected to be easier compared to the layering of glass powders or plates. The solution layers can be produced as thinly as desired. In this short six month period, we have synthesized the  $\text{TiO}_2\text{-SiO}_2$  sol-gel solutions for either step layering or continue layering. The composition gradient is formed in the layered sol-gel solutions. The sol-gel solution then is gelled and the composition gradient is kept. The wet gradient gels are dried and sintered at elevated temperature to form axis refractive index gradient glasses. The

experimental results clearly demonstrates the feasibility of fabrication of axial GRIN glasses via the layering of sol-gel solutions.

## 2. Objectives

The main objective of this Phase I project is to demonstrate the feasibility of fabrication of axial GRIN materials via the sol-gel process. In order to accomplish this goal, we have set the following objectives to be met in this project:

1. Examine and evaluate two methods to layer the solutions in term of ease of fabrication;
2. Prepare various metal alkoxide solutions, and colloidal solutions and investigate the properties of these solutions to facilitate the layering process;
3. Investigate the gelling, drying and sintering conditions of these layered sol-gel solutions;
4. Characterize the axial GRIN materials via the sol-gel layering;
5. Identify work to be performed in Phase II of the research.

### 3. Background

#### 3.1 Applications of Axial GRIN Glasses

Conventional optics are characterized by homogeneous materials which operate using Snell's Law. The surface shape is the parameter that controls its performance. Single optical components do not perform according to the first order theory thus causing aberrations. Several techniques have been developed and utilized to increase the number of adjustable parameters to control the aberrations that exist. These techniques include adding more lens elements, using nonspherical lens surfaces and using a lens with an inhomogeneous index of refraction. Among these three techniques, using a lens with an inhomogeneous index of refraction has an advantage since less lenses in a system are used provided the fabrication techniques have a reasonable cost of producing large gradient index lens blanks. Gradient index optics not only offer the possibility of replacing aspheric components or a number of conventional components with a single gradient component, but also provide some capabilities which are not available using conventional optics. By precisely and repeatably correcting for spherical aberration in the lens materials, axis GRIN lenses deliver optical performance superior to that of the best aspheric and doublet lenses in a single, spherically surfaced lens. These lenses are particularly well suited for use in high-performance laser based systems because of their diffraction-limited focusing performance, high power-handling capability, and low surface scatter.

A GRIN material is one which has a refractive index profile. The index profile of the GRIN can be represented by an index polynomial:

$$N(r,z) = N_{00} + N_{01}z + N_{02}z^2 + \dots + r^2\{N_{10} + N_{11}z + N_{12}z^2 + \dots\} \\ + r^4\{N_{20} + N_{21}z + N_{22}z^2 + \dots\} + r^{2p} N_{pq}z^q + \dots \quad (1)$$

where  $z$  is the coordinate along the optical axis and  $r$  is the radial coordinate. The axial GRIN, is represented by equation (1) by eliminating all terms which include  $r$  (Fig. 1). Fig. 2 schematically illustrates the correction of spherical aberration using an axial GRIN profile. An axial GRIN profile in combination with a spherical surface is virtually equivalent to an aspheric surface, with the refraction varied across the aperture by a local change in refractive index (Fig. 1).

The calculations on optical design of collimators indicates that using a single axial GRIN results in a wave-front error of less than 1/100 while using three to four homogeneous lenses only produces a performance of 1/20 [16]. A single element collimator in a compact disc system [17] which used an axial GRIN with a linear index profile was successfully fabricated by showing a rms wavefront error of 0.021 waves rms. The lens had a focal length of 17 mm and a numerical aperture of 0.17. The prototype was fabricated with an aperture of 5.5 mm and an index distribution depth of less than 0.5 mm with a  $\Delta n$  of 0.017.

Another successful application is to replace the objective of the M-19 binocular with a GRIN objective by using axial GRIN profiles [18,19]. Axial GRIN lens blanks were fabricated by traditional ion exchange technique ( $Ag^+$  for  $Na^+$ ). These axial GRIN lenses were used in the M-19 binocular objective (Fig. 3). If homogeneous objectives are used, three lenses have to be used. However, two axial GRIN objectives are able to achieve the same effect.

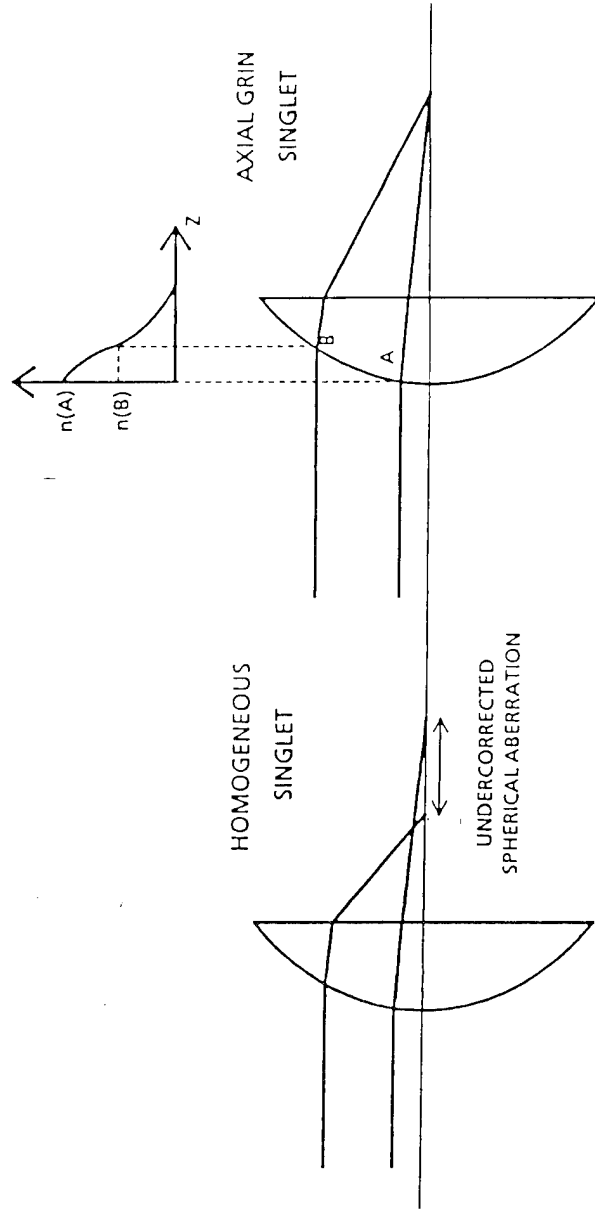
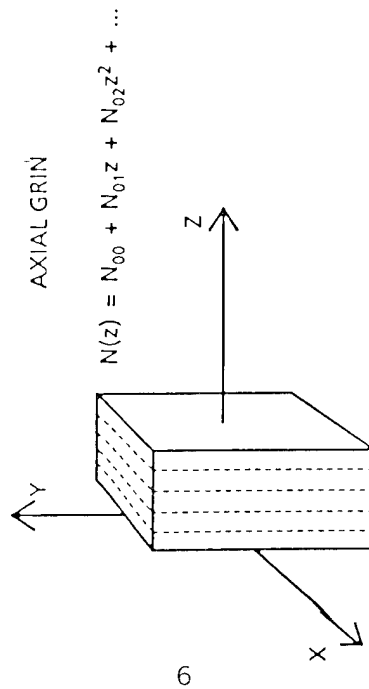


Fig.1 Axial GRIN Profile Geometry

Fig.2 Spherical aberration in a homogeneous singlet with spherical surface (a).  
Correction of the aberration using an axial GRIN profile (b).



Axial gradient-index elements were also found to be useful in both fixed and scanning eyepiece designs [20]. The additional degrees of freedom associated with the gradient made it possible to increase the half-fields of view of these eyepieces to  $25^\circ$  and extend the eye reliefs to 12 mm.

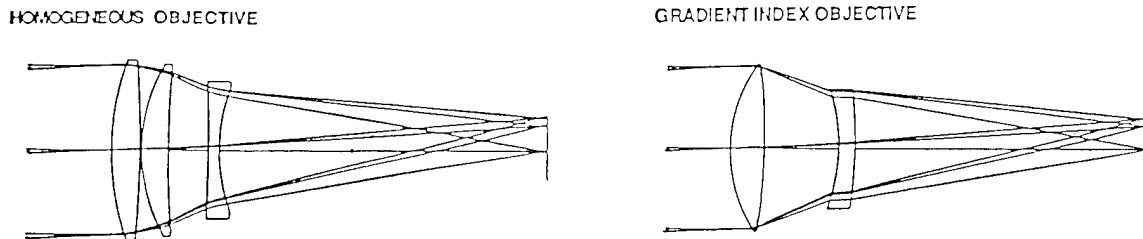


Fig.3 Layouts of the M-19 binocular objective. Left: original three element homogeneous objective, right: two element axial GRIN objective

Recently, axis GRIN glasses have been explored to be used in slide projectors in Eastman Kodak Co. [21] and night-vision systems [22].

The single-lens, diffraction-limited focusing performance of AGRIN lenses is the most notable benefit for laser system terms. Micron-scale spot size enhances wavefront quality, improves waveguide coupling efficiency, and increases beam-energy densities for a variety of coherent optical devices. An  $f/2.5$  AGRIN singlet places 82% of its incident power at 632.8 nm within a  $4 \mu\text{m}$  spot. By comparison, a computer-optimized cemented doublet can only place 25% of its incident energy in the same area. The pinpoint focusing capabilities of AGRIN lenses makes them ideal for fiber and waveguide applications. The focusing performance of positive AGRIN lenses results partly from their inherently better ability to control higher-order aberrations than single-surface aspherics. This is because the lens exposes two spherical correction for both surfaces. Thus, every AGRIN optic is functionally equivalent to an ultrahigh-quality biaspheric element. In addition, AGRIN lenses are notable for minimizing coma. Singlet optics available have  $+0.5^\circ\text{C}$  field of view, making them relatively easy to align in optical assemblies. The shape factor for these lenses is chosen to minimize third-order coma, then the gradient is applied to minimize spherical aberration. Real ray optimization balances higher-order aberrations. The AGRIN lens technology has the following advantages:

**Power Handling.** Cemented doublets are often used to correct for aberration in laser systems, but the relatively low damage threshold of the cement material can cause performance concerns. AGRIN lenses provide the same functionality as a doublet in a solid piece of glass, which makes them suitable for high-power lasers such as Nd:YAG laser systems. A comparison of laser damage thresholds reveals that AGRIN optics can be used safely at  $20 \text{ J/cm}^2$  for a 10-ns pulse at  $1.06 \mu\text{m}$ , ten times the safe energy level of a typical cemented doublet.

**Scatter.** Low surface scatter is critical in systems with a high number of optical elements, systems using high-power beams, a scatter-sensitive applications such as particle counting and flow cytometry. Because AGRIN lenses have spherical surfaces, they can be super-polished and easily test-plate fitted using conventional production methods. The

resulting lenses have far lower scatter and higher surface accuracy than the best hand-figured aspheres, molded glass lenses, and plastic aspheres.

**Reduction of Optical Elements.** The ability to provide spherical-aberration correction in a single lens means AGRIN lenses have potential for reducing the total number of optical elements in any optical system. Fewer optical elements means more efficient light transmission, lower Fresnel losses, and less scattering. Thus, the optical systems can be made into smaller, lighter, and less complex. Fewer optical elements in a design also has beneficial consequences for manufacturability; AGRIN lenses can significantly reduce design, fabrication, and alignment costs.

### 3.2 Present Axial GRIN Fabrication Technologies and Their Limitation

Numerous techniques have been used for manufacturing index-of-refraction variations in glasses and plastics. They include ion exchange, ion stuffing, fusing glass layers, etc. Table 1 lists the techniques for manufacturing gradient-index materials as well as the depth of the gradient and  $\Delta n$ 's. All these techniques can be used to make axial GRIN materials.

**Table 1 Techniques for Manufacturing Gradient-Index Materials**

Method	Size (mm)	$\Delta n$
Neutron irradiation	0.1	0.02
Chemical vapor deposition (CVD)	0.1	0.01
Polymerization	100.0	0.01
Ion exchange	10.0	0.04
Ion stuffing	50.0	0.04
Crystal growth	20.0	0.05
Fusing glass layers	25.0	0.50

#### Ion Exchange in Glasses

The most common method to make GRIN materials is cationic diffusion from a molten salt into a batch-melted glass. Ion exchange is best done with glass modifiers, both to preserve the structural integrity of the glass and to take advantage of their mobility in the glass network. The index distribution is dependent on the interdiffusion coefficient. Diffusion times from 15-72 hours are typical with diffusion depths of as much as 10 mm.

This technique is the simplest technique in term of instrumentation and control. However, it has a rather limited scope in terms of the profiles that can be manufactured. The profiles are limited to Gaussian, Lorentzian, and linear shapes. The limiting feature is the depth of 10 mm. In addition, the diffusions are too slow for the large diffusion depths required in GRIN systems to be practical. Grinding and polishing are still needed.

#### Molecular Stuffing [6]

A special glass which will undergo a phase separation at an elevated temperature is used as the base glass for GRIN materials via molecular stuffing. After phase separation, one of the phases is dissolved by an acid leaving porosity in the glass. These porous glasses are then placed in a salt bath where ions or molecules diffuse into the voids of the glass sponge. After the gradient is built up, the glass is recondensed by heating. This technique offers a possibility of large ions in the glass. However, if the phase separation is not uniform, the gradient is not uniform. Similar to the ion exchange technique, there are only limited types of profiles that can be created.

### **Chemical Vapor Deposition**

The chemical vapor deposition (CVD) technique has been widely employed in the manufacture of gradient-index fibers with a  $\Delta n$  of 0.01/100 mm for use in telecommunications [23]. Hamblen has used the CVD technique to codeposit of ZnSe and ZnS to produce axial index gradients in the range from 0.024 to 0.066/mm over a thickness of 4 mm [9]. The major issues that remain are nonuniform growth of the deposited material and limitations for preparation of large-geometry lenses.

### **Crystal Growth [11]**

To grow single crystals containing index of refraction gradients the materials used must be miscible in both the solid and liquid phases. The crystal structure and lattice constants of the constituents must be the same to prevent the creation of strains. Single crystals of sodium chloride, doped with silver chloride, have been grown as have germanium/silicon alloys. In the germanium/silicon system, limits in alloy composition of about 10% restrict the index gradient produced to about 0.05. The index gradients occur in the refractive index range from 3.65 to 4.0 for operation in the infrared. However, the single crystal is normally costly and the single crystal GRIN will be more costly due to the change in conditions during growth.

In addition to the techniques discussed above, neutron irradiation [8] and the photochemical process [24] have been employed to make GRIN materials. In neutron irradiation, a boron-rich glass is bombarded with neutrons to create a change in boron and thus a change in the index of refraction, while in the photochemical process the monomer of organic material is differentially changed into a polymer by irradiation of UV light. However these two techniques have not yet produced commercial GRIN materials.

### **Fusing Glass Layers for Axial GRIN Glasses**

Recently, a process [12-15] to produce gradient refractive indices in glass lens blanks of macro size and with  $\Delta n$  values up to  $\sim 0.5$  has been reported. The process is based on the controlled fusion of glass layers having the required gradient variations, and controlled diffusion within and between the layers. The concept proceeds by choosing glass composition candidates that can span the desired range of the index of refraction with little variation in their coefficients of expansion. During fusion and subsequent heat treatment, interfaces between layers are eliminated and a gradual transition in index, as well as properties, occurs. The glass layers were prepared by two methods. The first one is to select two glasses with the close thermal expansions, ground the glasses into powders, mix together in designed ratios for different layers, and then fuse them. The

second one is to stack glass plates and then fuse them. Fig.5 shows the linear gradient index profile of a GRIN blank. This technique presents a new concept of layering engineering. However, since the glass powders are large (tens of microns) or the glass plate are thick (0.1 mm), the homogenization requires long distance diffusion between layers and the diffusion is hard to control. Homogeneity at the molecular level is still questionable although this is a must for optical applications. Preparation of glass layers requires extensive grinding and polishing which greatly increases the cost of the manufacture of GRIN materials. Furthermore, grinding and polishing are still needed to fabricate desired shape of GRIN lenses. The most severe limitation in this technique is that it can not be extended to make micro-optical GRIN lenses or arrays.

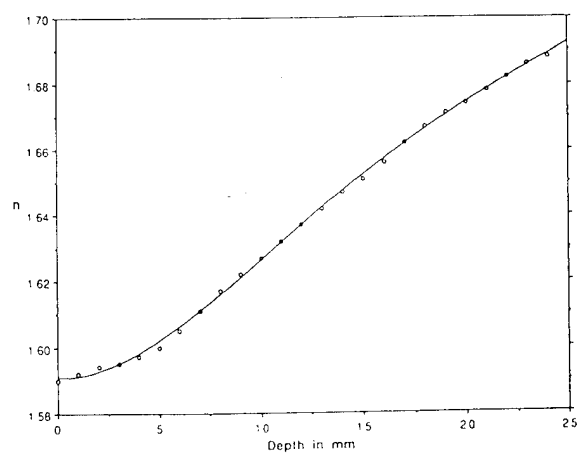


Fig. 5 Gradient profile of a GRIN blank

### Sol-Gel Radial GRIN Glass

The sol-gel method is a new technique for fabricating GRIN glasses. The method involves the synthesis of a wet gel, which is shaped by a mold. The wet precursor gels for GRIN form by either a colloidal silica process or hydrolysis and polycondensation of metal alkoxides. The gel is porous, so that dopants such as Tl, Cs, Ti, Pb which are used to modify the refractive index can be introduced (or removed) rapidly by immersing the gel into a solution containing the dopants (or acids for leaching). The doped (leached) gel is then dried and consolidated to form a clear GRIN glass without changing the concentration profile of the cations. This method has two major advantages over ion exchange in glasses: first, diffusion or leaching is conducted in a porous gel which makes for large GRIN profile depths since the transport is rapid. Second, a large variety of materials can migrate through the gel pores. Unlike ion exchange where one is for all practical purposes limited to univalent cation exchange, molecular species and bivalent ions such as Pb are easily transported through the gel pores.

Yamane, et al. in 1986 reported making GRIN materials via the sol-gel process [7]. A gel formed in a mold by hydrolysis and polymerization of silicon alkoxide with boron oxide precursor and an aqueous metal salt solution. The gel is then immersed in a solution containing another species of metal salts which exchanges with the constituent metal salts. After diffusion, the gel is dried and sintered to yield a GRIN glass. A 6 mm diameter radial GRIN rod was fabricated with a  $\Delta n$  of 0.016 by exchanging  $Pb^{2+}$  ions

with  $K^+$  ions in the gel diffusion stage. However migration of lead ions toward the surface during drying of the gel decrease the  $\Delta n$  in spite of the introduction of large amounts of lead. The ability to control the profile shape is crucial and can be difficult.

An alternative method is acid leaching of bound dopant [25,26]. Two binary systems,  $Si(OCH_3)_4-Ge(OC_2H_5)_4$  and  $Si(OCH_3)_4-Ti(OC_4H_9)_4$  have been investigated. Immersion of rod-shaped wet gels in neutral or acidic water gives rise to leaching of the dopants (germanium and titanium components), building up concentration gradients. Radial GRIN rods of about 2 mm in diameter and 20 mm in length having  $\Delta n$  of about 0.02 have been fabricated. The resolution of the lens was evaluated as  $> 100$  lines/mm. The GRIN lens shows high coupling efficiency with optical fibers as well as good beam collimation properties and enables a low-loss large-distance space transmission of light between optical fibers.

Caldwell et al. [27] studied refractive index profile reproducibility on the  $TiO_2-Al_2O_3-SiO_2$  system. The radial GRIN glass rod obtained by casting a sol into a tube of 15 mm inside diameter to the length of 96 mm was about 5 mm in diameter and had a parabolic index profile with  $\Delta n$  of 0.03. The index profile variation is equivalent to those by ion exchange techniques. Further optimization developed a high titania ternary system which produced 6 mm diameter lenses with  $\Delta n$  up to 0.07 [28]. The commercialization of sol-gel derived radial GRIN lenses is expected in the near future.

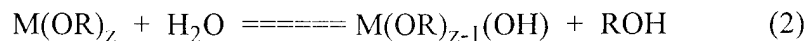
### 3.3 Sol-Gel Technology

#### The Principle of the Sol-Gel Technology

The preparation of inorganic materials via chemical routes is not new but currently it is treated as modern technology. The sol-gel technology is one of these routes. Several commercial products have been developed up to now e.g. silica optical lenses, antirefraction coatings, and Nextel fibers. The sol-gel process normally starts with a solution of metal organic precursors or inorganic precursors. In aqueous or organic solvents the precursors are hydrolyzed and polycondensed to form inorganic polymers, or gels, which composed of M-O-M bonds. Fig.6 shows a schematic illustration of the overview of the sol-gel process.

For inorganic precursors (salts), hydrolysis proceeds by the removal of a proton from an aquo ion  $[MO_nH_{2n}]^{z+}$  to form a hydroxo (M-OH) or oxo (M=O) ligand. Condensation reaction involving hydroxo ligands result in the formation of bridging hydroxyl (M-OH-M) or bridging oxygen (M-O-M) bonds depending on the coordination number of M and the acidity of the bridging hydroxyl. If peptized by the addition of acid or sterically stabilized by adsorption of organic molecules, these colloidal sols are able to form gels which can be subsequently converted into glasses by drying and densification.

The most commonly used organic precursors for sol-gel process are metal alkoxides  $(M(OR)_z)$ , where R is an alkyl group  $(C_xH_{2x+1})$ . Normally the alkoxide is dissolved in alcohol and hydrolyzed by the addition of water under acidic, neutral or basic conditions. Hydrolysis replaces an alkoxide ligand with a hydroxyl ligand:



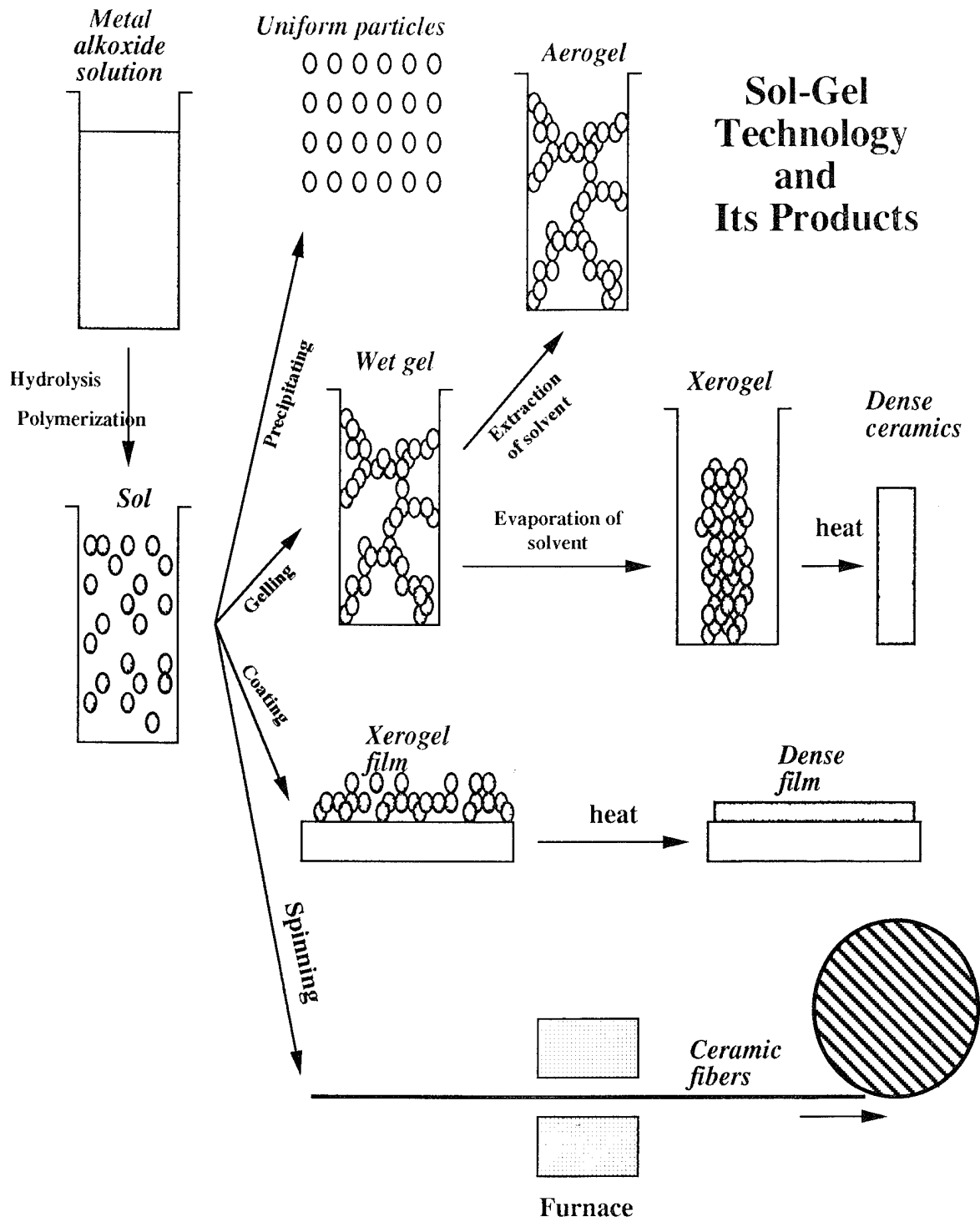
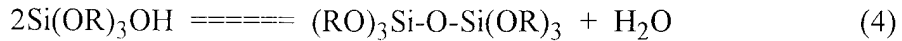
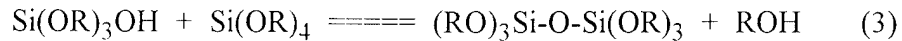


Fig.6 Overview of the sol-gel process

Condensation reaction involving the hydroxyl ligands produce polymers composed of M-O-M or M-OH-M bonds plus, in most cases, the by-products water or alcohol as shown below for silicate condensation:



Subsequent hydrolysis and polymerization reactions form a gel which contains a three dimensional metal oxygen network with water, solvent and residue OR groups.

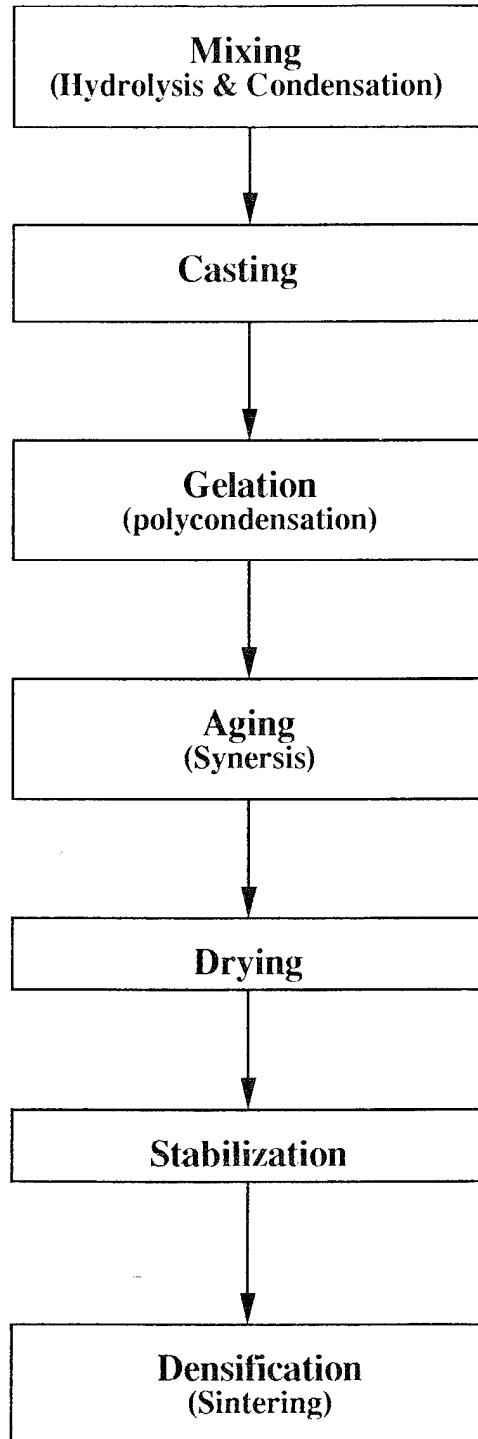
The residues (water, solvent and OR groups) in the wet gels are removed by drying. As this drying stage takes place the gel shrinks by a large amount until eventually it becomes a solid which has a very high level of porosity. Such a solid is called a XEROGEL. The usual way of carrying out this process is by very slow drying at ambient or slightly elevated temperature to avoid the cracks which are caused by capillary forces. In order to accelerate the drying process, drying control chemical additives (DCCA) in alkoxide sols have been used [29]. DCCA such as formamide ( $\text{NH}_2\text{CHO}$ ), glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) and oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) help produce a narrower pore size distribution, increase gel density, and increase strength. Thus it minimizes the capillary force and reduces cracking. Large xerogels of  $\text{SiO}_2$ ,  $\text{Li}_2\text{O-SiO}_2$ ,  $\text{Na}_2\text{O-SiO}_2$ , and  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  have been fabricated by employing DCCA [29]. If the wet gel is placed in an autoclave and dried under supercritical conditions, there is no interface between liquid and vapor, so there is no capillary pressure and relatively little shrinkage. This process is called supercritical drying, and the product is called an AEROGEL.

Xerogels and aerogels can be densified to produce glasses. The conditions of time and temperature of densification will depend very much on the original gel structure. In general, a feature of sol-gel processing is the fact that this densification takes place at a much lower temperature than one would require to make the equivalent materials by a conventional route: fusion of oxides to form a glass.

### **Fabrication of Optical Materials via the Sol-Gel Process**

Sol-gel processing of optical glasses was demonstrated by Professor Larry Hench and his co-workers [30]. They used DCCA to control the rate of hydrolysis and condensation, pore size distribution, pore liquid vapor pressure, and drying stresses. A wide range of sizes and shapes of optically transparent dried gel monoliths of  $\text{SiO}_2$ ,  $\text{Li}_2\text{O-SiO}_2$ ,  $\text{Na}_2\text{O-SiO}_2$ , and  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  and other glasses have been made. The sol-gel  $\text{SiO}_2$ /DCCA process is illustrated in Fig.7. The resultant silica-gel glass samples demonstrate a uniformly high transmittance in the 200 - 2600 nm (UV-VIS-NIR) range, and exhibit no absorption throughout the 200 - 2600 nm range. In contrast, Corning 7940 and NSG-ES silica glasses have absorption peaks at 1370 nm and 2200 nm. The glass refractive index of these silica-gel samples are about 1.460 - 1.475 depending on the wavelength.

Up to now, the  $\text{SiO}_2\text{-TiO}_2$  glass system is one which has the highest refractive index among the sol-gel derived optical glasses. Yoldas [31] used the metal alkoxide sol-gel approach to form titania-silica glasses. The monolithic materials are derived from



**Fig. 7** Fabrication of silica glasses via the sol-gel process



tetrathoxysilane,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , and titanium ethoxide,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . TEOS is partially hydrolyzed with one mole of water in ethyl alcohol, and then the titanium alkoxide is introduced into the solution under vigorous stirring. The polymerization with other silanols occurs with aging and finally leads to formation of a three dimensional metal oxide network, i.e. a gel. Heating to  $500^\circ\text{C}$  causes the system to be free from all the organic components, leaving behind an inorganic glass. Further high temperature heat treatment densifies the glasses. The refractive indices of the entire  $\text{SiO}_2$ - $\text{TiO}_2$  binary coatings derived from the sol-gel solutions is shown in Fig.8. The refractive indices change from 1.4 for pure  $\text{SiO}_2$  to above 2 for pure  $\text{TiO}_2$ .

Sakka and Kamiya [32] also used the similar approach to make  $5.0\text{TiO}_2$ - $95\text{SiO}_2$  and  $7.9\text{TiO}_2$ - $92.1\text{SiO}_2$  glasses with thickness of 4 mm. The drying took about 4 months and then the dry gels were fired at  $900^\circ\text{C}$  with a heating rate of  $6^\circ\text{C}/\text{hr}$ .

A series of bulk glasses in the  $\text{SiO}_2$ - $\text{TiO}_2$  system have been prepared by Hayashi et al. [33] via the hydrolysis of the mixture solution of  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  and  $\text{Si}(\text{OC}_2\text{H}_5)_4$  with water and HCl, and slowly heating the resultant gels up to  $800^\circ\text{C}$ . The properties of  $\text{SiO}_2$ - $\text{TiO}_2$  glasses obtained by the gel method in the less than 12.9 wt%  $\text{TiO}_2$  range obtained were very similar to those of oxide glasses made by the flame hydrolysis process (Fig.9). In the less than 10.4 wt%  $\text{TiO}_2$  range, the glasses obtained by heating up to  $800^\circ\text{C}$  did not crystallize at  $1000^\circ\text{C}$  or higher, while in the more than 20 wt%  $\text{TiO}_2$  range anatase was precipitated at  $900^\circ\text{C}$ .

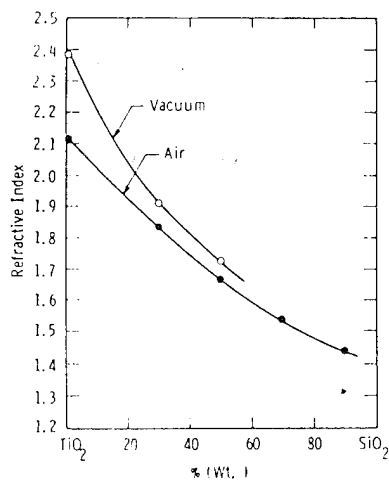


Fig.8 Index of refraction of coatings

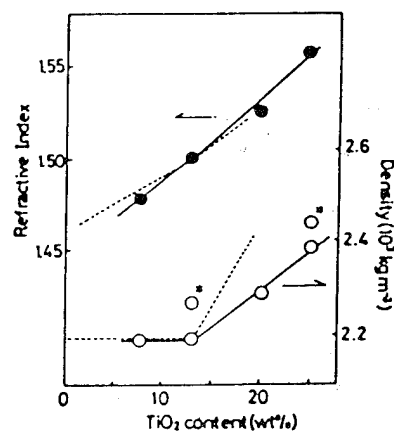


Fig.9 Refractive index of  $\text{SiO}_2$ - $\text{TiO}_2$  glasses

Satoh et al. [34] have prepared doped silica glasses,  $\text{SiO}_2$ - $\text{MO}_{n/m}$  ( $M = \text{Ga}, \text{Gd}, \text{Nb}, \text{Sb}, \text{Sn}, \text{Ta}, \text{Ti}$  and  $\text{Zr}$ ) by the sol-gel process. These dopings were selected based on the following criteria: (1) high refractive indices on the basis of Appen's empirical law; (2) element stability in the  $\text{SiO}_2$  network and the doped glasses' durability in the ambient atmosphere; (3) expected low optical losses; and (4) non-toxicity of doped glasses. A mixture of tetramethoxysilane,  $\text{Si}(\text{OCH}_3)_4$  and dopant metal alkoxide, water and alcohol of a given molar ratio was cast in glass containers. After aging and drying for about a week, porous gel bodies of 4 -6 mm in diameter and 100 mm in length were obtained. The gels were sintered under a constant heating rate of  $0.02 - 0.06^\circ\text{C}/\text{s}$  up to  $700^\circ\text{C}$  in an  $\text{O}_2$  or  $\text{O}_2 + \text{He}$  atmosphere and then up to  $1100^\circ\text{C}$  in a He or He +  $\text{O}_2$  atmosphere to

obtain glasses. Doped silica glass samples about 4 mm in diameter were obtained. The refractive index of doped silica glasses is shown in Fig. 10. Refractive indices of Ga-, Ta-, Zr- and Ti-doped glasses increase linearly with dopant concentrations, whereas those of Nb-, Sb- and Sn-doped glasses do not. Of these systems, the Nb and Sn systems crystallized. Zr-, Ti- and Ta-doped systems have the largest increase in refractive indices over per mole percent.

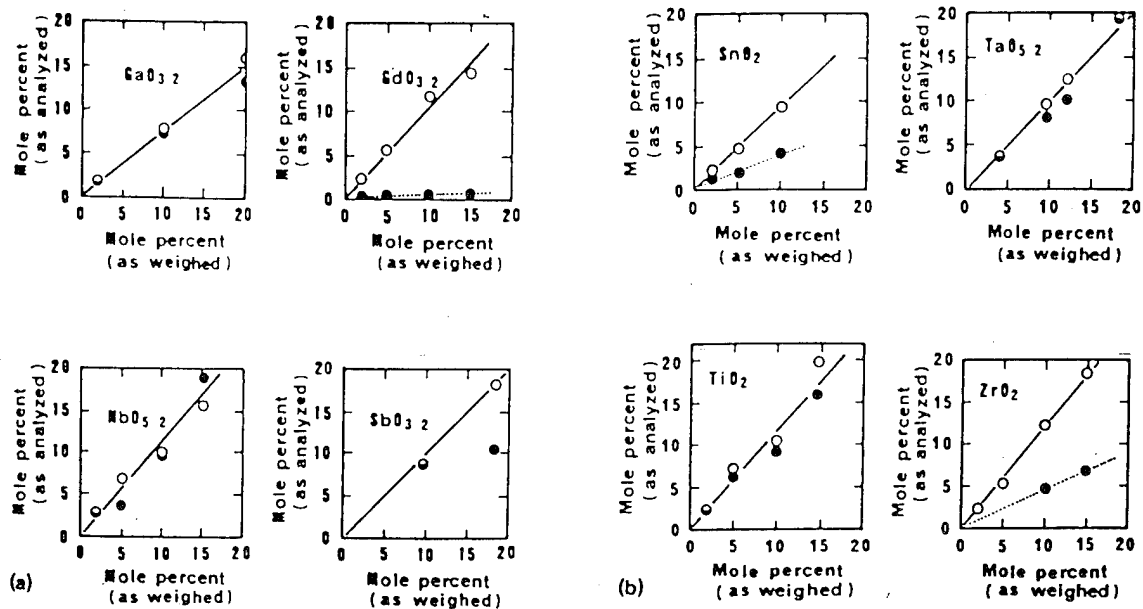


Fig.10 Compositional change of dopant metal (a)Ga, Gd, Nb and Sb and (b) Sn, Ta, Ti and Zr, in the gels (o) and glasses (o)

In Konishi's preparation of  $\text{TiO}_2\text{-SiO}_2$  radial GRIN [35], silicon tetramethoxide  $[\text{Si}(\text{OCH}_3)_4]$  was partially hydrolyzed. Then titanium n-butoxide  $[\text{Ti}(\text{OC}_4\text{H}_9)_4]$  was added to the solution while stirring vigorously. Formamide ( $\text{HCONH}_2$ ) was introduced as DCCA. Rod-shaped wet gels were obtained after a few hours. The aged gels were immersed in a HCl solution to leach out the titanium component. Then the leached wet gels were immersed in a methyl alcohol solution of 30 vol% formamide. The dry gels were obtained by heating the wet gels up to  $140^\circ\text{C}$  in open air. The dry gels were then heated to  $800^\circ\text{C}$  in an oxygen gas atmosphere to remove absorbed water and organic residues. Finally, the gels were heated up to  $1250^\circ\text{C}$  in a helium to obtain the densified glasses of 2 mm in diameter and 5-10 mm in length.

In Caldwell et al.'s process [36] for  $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$  radial GRIN, 0.796 moles of tetramethoxysilane (TMOS) were added to a solution containing 4.723 moles of methanol and 2.47 moles of N,N-dimethylformamide. 14.4 ml of HCl were added to the reaction mixture and then a mixture consisting of 0.046 moles titanium isopropoxide  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  and 0.094 mole of aluminum di(sec-butoxide) acetoacetic ester chelate was added. The hydrolysis and polycondensation reactions were allowed to proceed for one hour. Finally 2.98 moles of water were added to complete the reaction. Gelation occurred within several hours at room temperature, and the wet gels were aged for 2 days. The

leaching was done with 3.0 M aqueous  $H_2SO_4$ , and then the gels were "fixed" with methanol. The gels were then dried and calcined in a box furnace. Finally the fired samples were densified at  $1500^\circ C$ .

It is known that a colloidal sol-gel process can also be used to make the optical glasses [37]. This approach minimizes cracking during drying, but needs high temperatures to densify the porous glasses. Zaide Deng, et al. [38] have used this approach to make a series of  $TiO_2/SiO_2$  glasses with 0 - 9  $TiO_2$ . The sol was prepared by dispersing colloidal silica fume in an aqueous solution of titania which was synthesized through the acid-catalyzed hydrolysis of titanium isopropoxide. The sols gelled in 2-4 days, and then were dried for 6 - 8 days. The dry gels were sintered at  $1450^\circ C$  -  $1500^\circ C$  to produce clear, dense, microstructure-free glasses. The gels underwent a total shrinkage of ~50% to yield glass rods about 50 mm long and 5 mm in diameter, or glass discs about 4 cm in diameter and 5 mm thick. The drying step was most critical in the production of crack-free specimens. In the gel, transmission electron microscopy (TEM) revealed the presence of 1 - 5 nm rutile microcrystallites uniformly distributed within a network of colloidal silica particles. After sintering to 1450 -  $1500^\circ C$ , transparent, microstructure-free glasses were created. Fourier transform infrared spectroscopy (FTIR) verified the formation of an amorphous solid-solution of titania and silica after sintering.

The sol-gel process, in addition, allows molding of pieces with complex geometries such as aspheric optics and lightweight mirrors. Net shape casting and high quality surface finishes are possible requiring little or no grinding and polishing. Complex surface structure such as Fresnel lenses can be accurately reproduced [39].

#### 4. Phase I Results

In Phase I research, we have met the following goals to demonstrate the feasibility of fabrication of axial GRIN materials via the sol-gel process:

- a. Examining and evaluating two methods to layer the solutions in term of ease of fabrication:

Continue layering has been identified to be ease in the formation of the gradient sol-gel solutions.

- b. Identifying, preparing sol-gel solutions and investigating the properties of these solutions to facilitate the layering process.

Two stable and compatible solutions:  $SiO_2$  and 83 mole% $SiO_2$  - 17 mole% $TiO_2$  sol-gel solutions have been identified and synthesized.

- c. The axis GRIN wet gels, dried gel glasses and sol-gel glasses have been fabricated.

The maximum refractive index change ( $\Delta n$ ) achieved is about 0.1.

In Phase I, we prepared various  $SiO_2$  and  $SiO_2-TiO_2$  sol-gel solutions and tested their compatibility between these two solutions. Two stable  $SiO_2$  and  $SiO_2-TiO_2$  sol-gel solutions have been identified to be compatible with each other without any precipitation, thus they have been used as the layering solutions to form an axis  $SiO_2-TiO_2$  composition gradient solution. The two layering techniques: step layering and continue layering, have been evaluated in term of ease of the fabrication of the gradient solution. Both of these two layering techniques give the composition gradient in the  $SiO_2-TiO_2$  sol-gel solutions.

The continue layering technique is favored because only two solutions are used, compared to that many solutions with different compositions have to be used in the step layering technique, and the gradient is continuously forming. The gradient is kept while the solution gelled, dried and sintered. The refractive index distribution is linear, and the maximum refractive index change ( $\Delta n$ ) achieved is about 0.1.

#### 4.1 Preparation of the SiO<sub>2</sub>-TiO<sub>2</sub> Sol-Gel Solutions

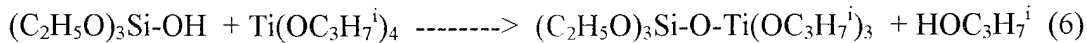
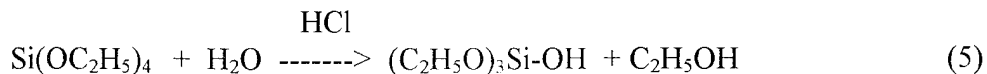
The SiO<sub>2</sub>-TiO<sub>2</sub> system was chosen as the system to demonstrate the feasibility of the proposed process since this system has been investigated in more detail than other binary system and also the introduction of TiO<sub>2</sub> can greatly increase the refractive index of the materials. To make axial GRIN materials, we have investigated two types of SiO<sub>2</sub>-TiO<sub>2</sub> sol-gel solutions which are metal alkoxide sol-gel solutions and colloidal sol-gel solutions.

##### a. Metal Alkoxide Sol-Gel Solutions.

The precursors for SiO<sub>2</sub> and TiO<sub>2</sub> via the sol-gel process are silicon alkoxides (e.g. Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) and titanium alkoxides (e.g. Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>). The hydrolysis and polycondensation rates of these alkoxides are dramatically different from each other. It is necessary to add the catalyst such as HCl or NH<sub>4</sub>OH to the Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> solution with water to hydrolyze Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. No hydrolysis occurs without catalysts adding into the Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> solution. In contrast, the water in air is able to hydrolyze Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>. The large difference in hydrolysis rate in these two types of alkoxides causes the problem in the layer solution compatibility. In this research, we have used two approaches to overcome this problem (Fig. 11).

##### The Partial Hydrolysis Approach

One of the approaches is to partially hydrolyze the Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> solution before the Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> solution is added. The purpose is to activate Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> by partial hydrolysis which will react with Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>:

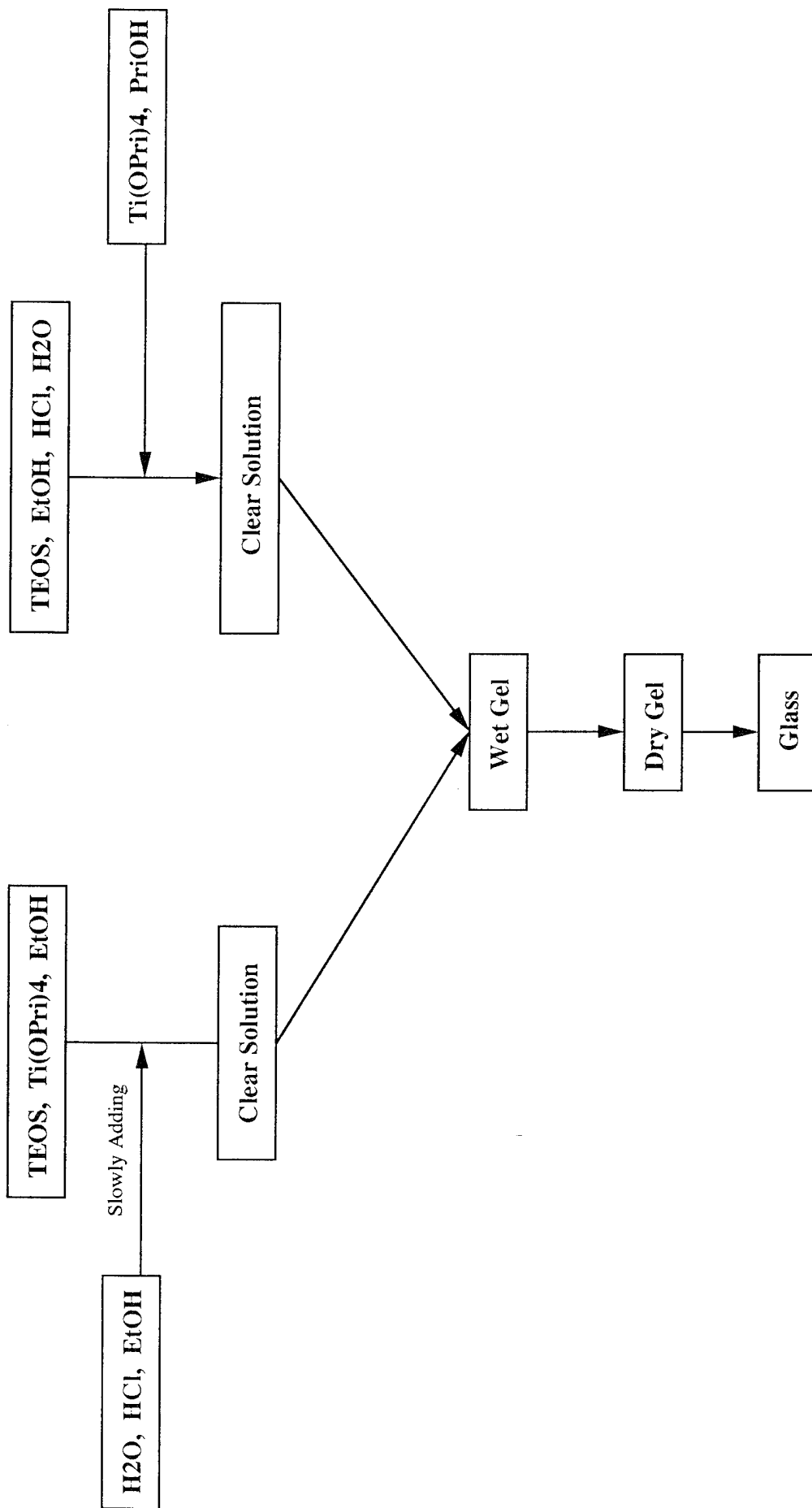


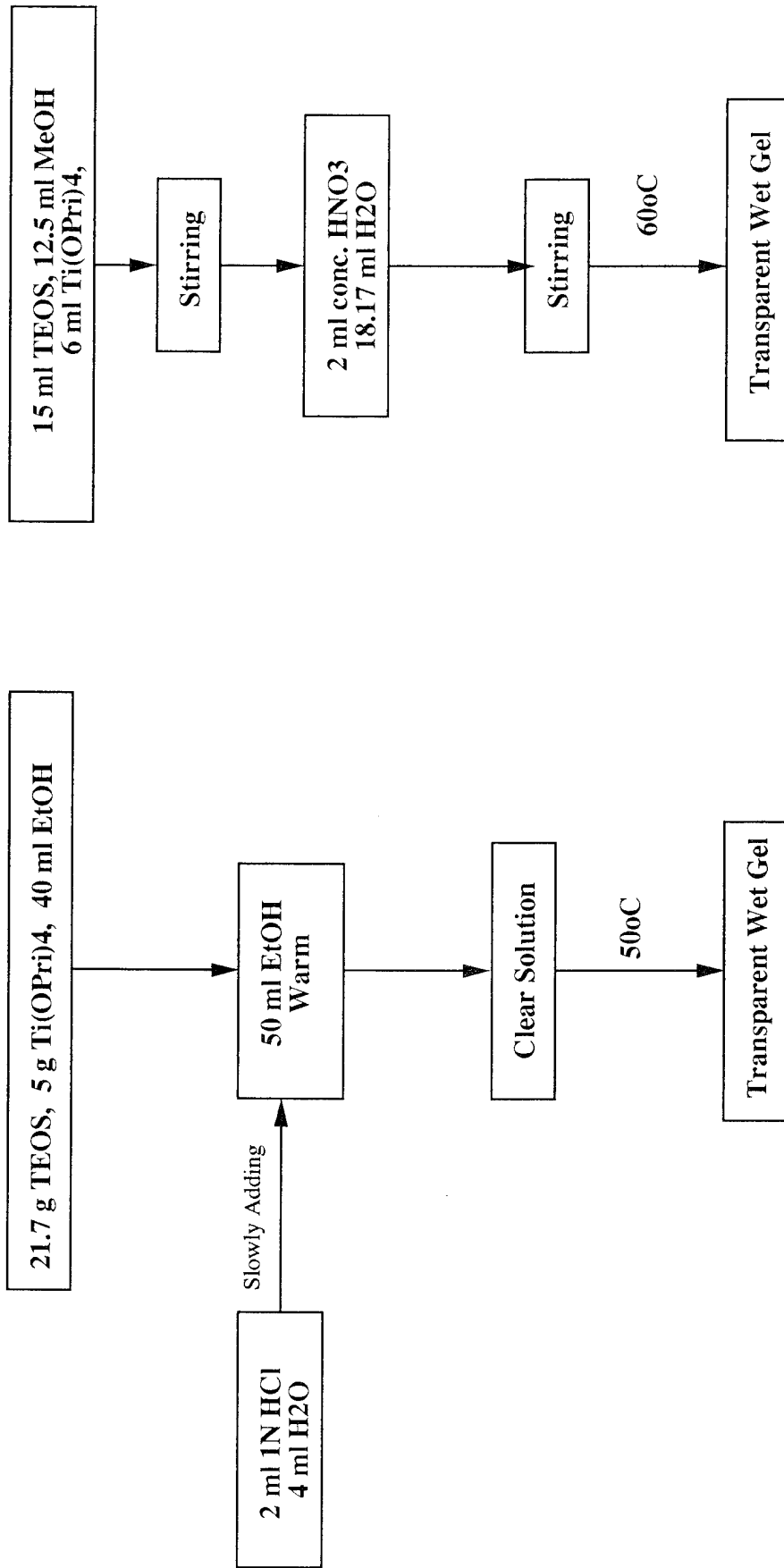
The new formed (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si-O-Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> species are used as precursors to minimize the difference in the hydrolysis rate of two types of metal alkoxides. Since the reaction (5) is slow, we have investigated the effect of addition of Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> at different times. Table 2 shows the experimental results. It is seen that the addition of Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> at the right time can minimize the precipitation, but it is hard to control. In addition, the homogeneity of the solution is questionable.

The second approach in this research is to hydrolyze both Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> and Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> at the same time at a slow hydrolysis rate (Fig. 11). Two solutions have been prepared without any precipitation. The procedures to make these two solutions are shown in Fig. 12. Both of these solutions are used for testing two layering techniques.

**Table 2 Compatibility Tests Between TEOS Solutions and  $\text{Ti}(\text{OPr})_4$  Solutions**

Sample	TEOS	HCl(1 N)	H <sub>2</sub> O	EtOH	Ti(OPr) <sub>4</sub>	Condition/Result
A	62.5 g	3 ml	18.6 g	17.7 ml	-	80°C, gelled in 3 hours; 60°C gelled in 7 hours
B1	62.5 g	3 ml	18.6 g	17.7 ml	9.38 g	Ti(OPr) <sub>4</sub> added in 1 hour, precipitate
B2	62.5 g	3 ml	18.6 g	17.7 ml	9.38 g	Ti(OPr) <sub>4</sub> added in 6 hours, precipitate
B3	62.5 g	3 ml	18.6 g	17.7 ml	9.38 g	Ti(OPr) <sub>4</sub> added in 18 hours, precipitate
C	62.5 g	3 ml	18.6 g	17.7 ml	9.38 g	Ti(OPr) <sub>4</sub> added in 10 hours after solution A in 40°C, small amount of precipitates





**Process One**

**Process Two**

**Fig.12** The synthesis procedures of stable, clear sol-gel TiO<sub>2</sub>-SiO<sub>2</sub> solutions

### b. Colloidal Sol-Gel Solutions.

In this approach, Zaide Deng's recipe has been employed. It uses colloidal silica fumes and titania colloids made from titanium isopropoxide. Both titania and silica colloidal solutions have been prepared via controlling the hydrolysis of titanium isopropoxide and silicon ethoxide. The stable silica-titania colloidal solutions with different ratios of  $\text{SiO}_2/\text{TiO}_2$  have been prepared. However, the solutions, the wet gels and the dried gel as well as sintered glasses are not transparent. Therefore, no more efforts have been placed in these solutions.

### 4.2 Formation of the Gradient via the Layering Techniques

Fabrication of glasses via the sol-gel process starts with solution, to wet gels, to dried gel glasses, finally to dense glasses. To make axial GRIN glasses, we started to make GRIN solutions which are prepared by two techniques (Fig. 13): (1) the step layering and (2) continuous layering:

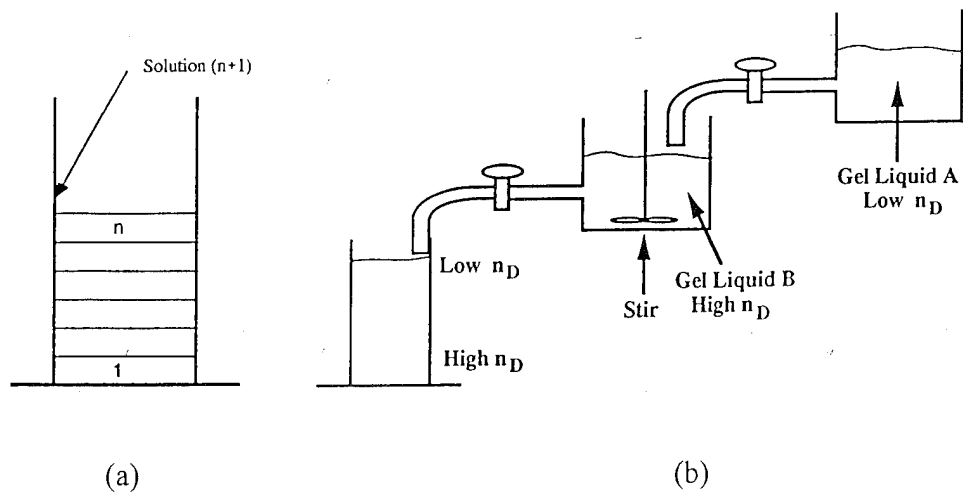


Fig. 13 Sol-gel layering techniques: (a) step layering; and (b) continuous layering

**a. Step Layering.** In this method, the solutions with different  $\text{TiO}_2/\text{SiO}_2$  ratios will be poured into the mold layer by layer. Fig. 14 is a photo of a layered  $\text{TiO}_2/\text{SiO}_2$  gel glass which are made up of the layers of  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-TiO}_2$ , . The clear boundary between the layered solution was observed, which indicates the feasibility of using the step layering technique to form the refractive index gradient in one hand, and the problem to control the diffusion of the solution in other hand. The refractive index of the solution is shown in Fig. 14.

**b. Continuous Layering.** In this method, two solutions, one of pure  $\text{SiO}_2$  and the other of  $\text{SiO}_2\text{-TiO}_2$  are simultaneously mixed and poured into mold, as shown in Fig. 13. The refractive index measurement of the solution at different position is shown in Fig. 15, which clearly demonstrates the linear distribution of the refractive index along the axis.



In summary, the continuous layering technique is favored since only two solutions are needed to be prepared and no strict control on diffusion is needed.

#### **4.3 Gelation, Drying and Sintering of GRIN Glasses**

The next several steps to prepare the glasses in the sol-gel process are gelation of the sol-gel solutions, drying the wet gels, sintering the dried gel glasses. All these steps have been well investigated in the past, and many techniques have been developed. In this research, we mainly focus on the demonstration of retaining the refractive index gradient which formed in the solution using layering techniques during these steps.

Fig. 16 shows the refractive index profiles in the solutions, wet gels, xerogel glasses and sintered glasses of the  $\text{SiO}_2\text{-TiO}_2$  system. It is seen that the refractive index increases from the solution to the glasses, and also refractive index change along the axis increases. In the glasses, the maximum refractive change is about 0.1 as expected.

#### **4.4 Characterization of Axial GRIN Materials**

**Transmission.** The sol-gel derived  $\text{SiO}_2\text{-TiO}_2$  GRIN samples are as transparent as normal glasses. Fig. 17 shows several GRIN samples.

**X-Ray Diffraction.** It has been found that  $\text{SiO}_2\text{-TiO}_2$  gel glasses will form crystallites when the  $\text{TiO}_2$  content is above 20 wt% in the  $\text{SiO}_2\text{-TiO}_2$  glasses (Fig. 18). This result agrees with reported data [33].

#### **5. Conclusion**

The goal of the Phase I research is to demonstrate the feasibility of fabrication of axial GRIN materials via sol-gel layering. In this short six month period, we have prepared various  $\text{TiO}_2\text{-SiO}_2$  sol-gel solutions for evaluation of their applicability in the layering process. Two types of the  $\text{TiO}_2\text{-SiO}_2$  sol-gel solutions have been identified to be the proper solutions for sol-gel layering. The two layering techniques proposed have been evaluated in this research, and the experimental results indicate that the continuous layering technique is favored due to its ease of formation of gradient solutions. Hundreds of the gradient solutions have been fabricated using these layering technique, and the experimental measurement proved the formation of the gradient. The gradient is retained during the gelation, drying and sintering. The refractive index increases along the process, from 0.01 to 0.1. The resultant refractive index distribution of the samples is linear, as expected. The maximum refractive index change is about 0.1 in the sintered glasses.

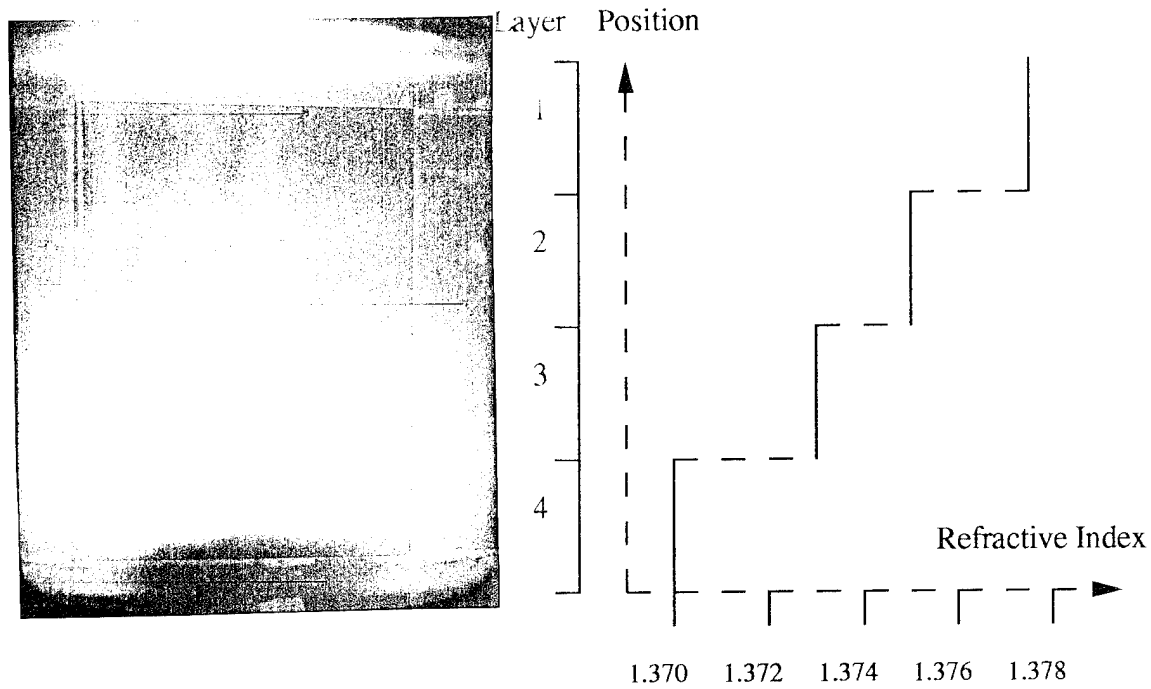


Fig.14 The photo of the step layered  $\text{SiO}_2\text{-TiO}_2$  wet gel and the corresponding refractive index of each layer

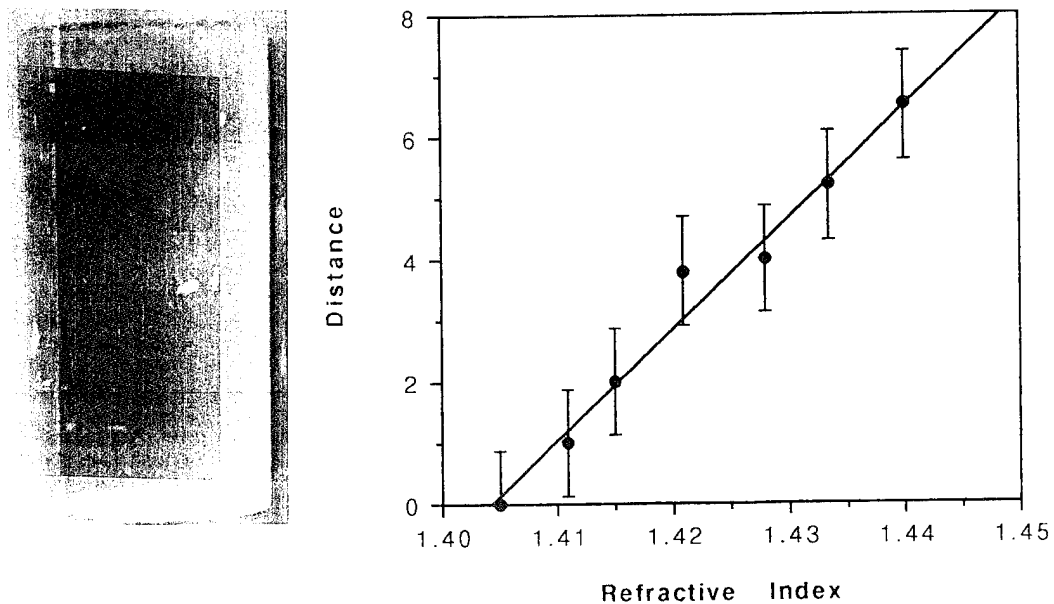


Fig.15 The photo of the continuously layered  $\text{SiO}_2\text{-TiO}_2$  xerogel and the corresponding refractive index

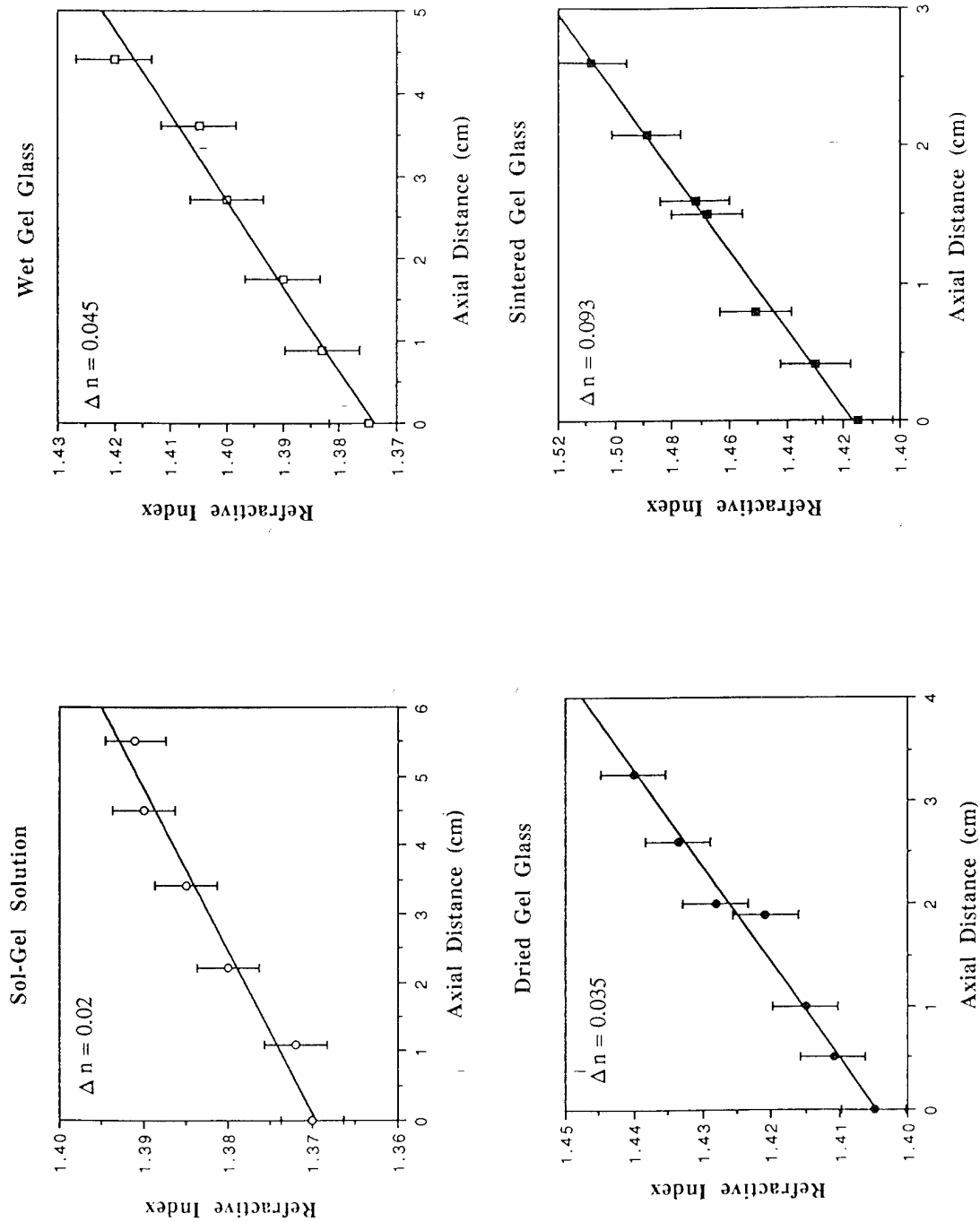
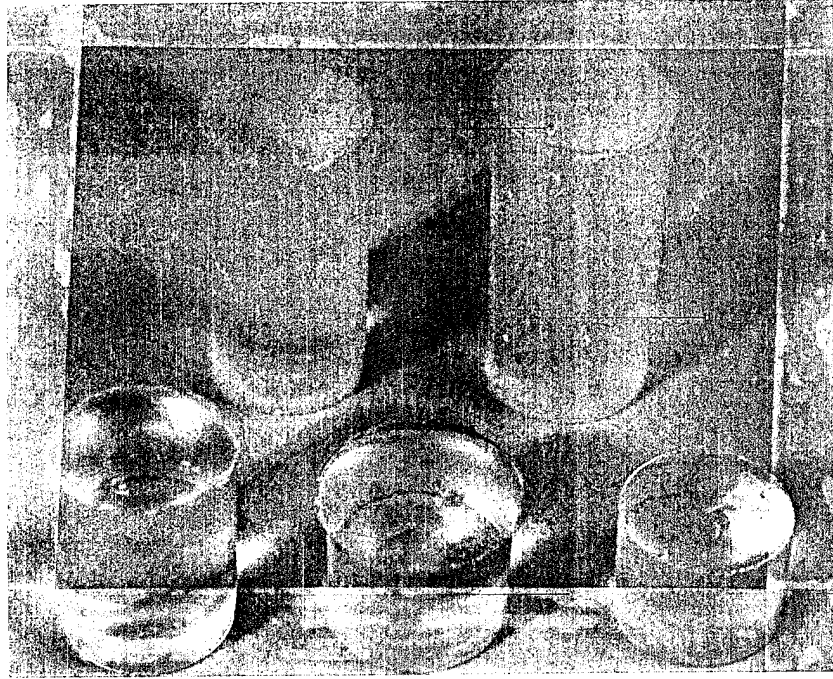
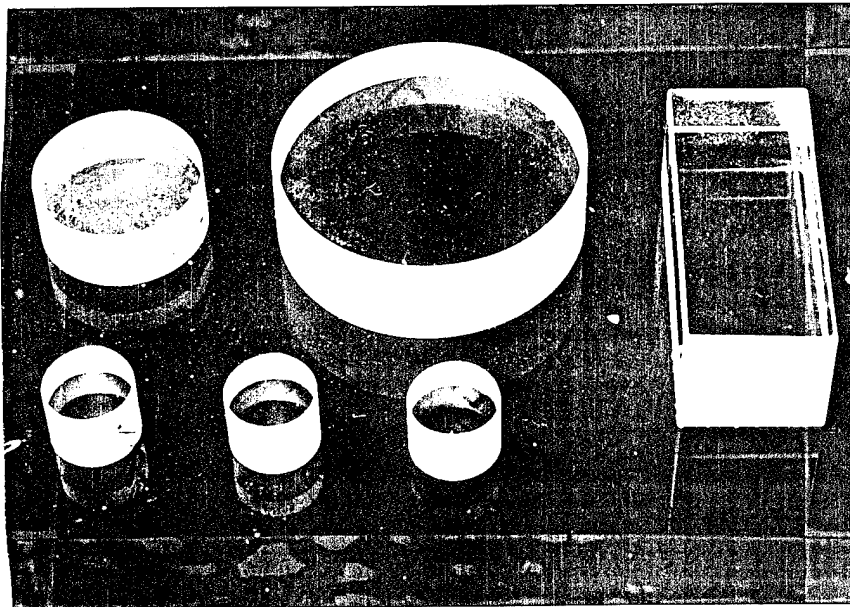


Fig. 16 The the refractive index profiles of the solution, wet gel, xerogel glass and sintered glass of the  $\text{SiO}_2\text{-TiO}_2$  glass system made by the continuously layering technique



(a) the dried xerogel axial GRIN glasses



(b) the sintered axial GRIN glasses

Fig.17 The axial GRIN glasses made from the sol-gel continuous layering technique. (a) the dried xerogel axial GRIN glasses; (b) the sintered axial GRIN glasses.

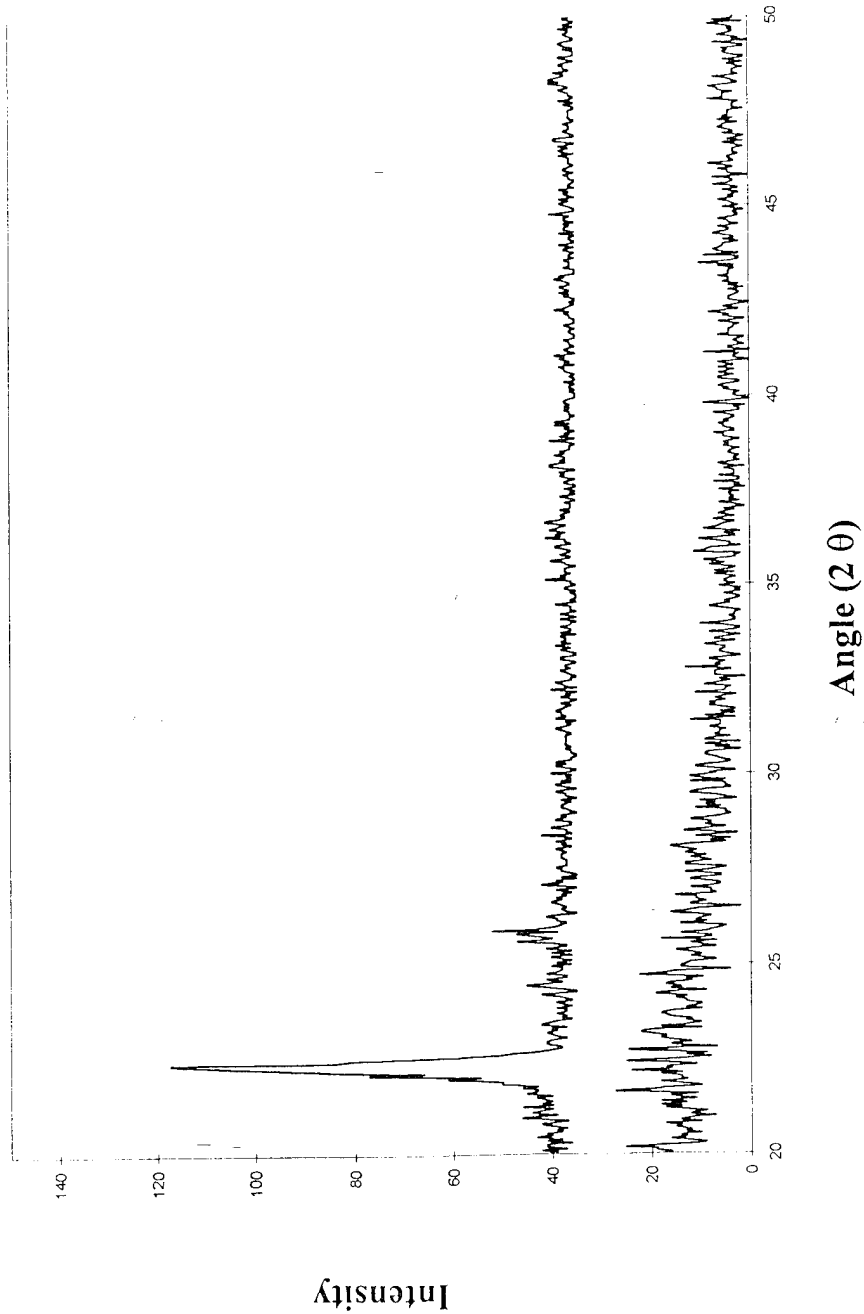


Fig.18 X-ray diffraction patterns of the sintered axial SiO<sub>2</sub> - TiO<sub>2</sub> GRIN glasses, 900°C for one hour . (Top: 83 mole%SiO<sub>2</sub> - 17 mole%TiO<sub>2</sub>; Bottom: SiO<sub>2</sub>)

## 6. Identification of Work for Phase II Program

The Phase I work has successfully demonstrated the feasibility of fabrication of axial GRIN materials via the sol-gel layering. The refractive index of the glasses changes from 1.4 to 1.6 along the axis. The profile of the refractive index is linear. These results clearly indicate the feasibility of practical applications of the sol-gel derived axial GRIN glasses. In order to facilitate the application this novel optical glass component, the following tasks have been identified to be carried out in Phase II:

- A. Fabrication of GRIN glasses with diverse compositions to cover all requirements in the optical design;
- B. Set up a pilot plant to test production of the GRIN glasses;
- C. Identification of the first application for GRIN glasses, and fabricate the first optical system which employs the GRIN glasses.
- D. Develop a business plan for commercialization

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