

# PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://spiedigitallibrary.org/conference-proceedings-of-spie)

## Recent Progress In Gradient-Index Optics

Susan Houde-Walter

Susan Houde-Walter, "Recent Progress In Gradient-Index Optics," Proc. SPIE 0935, Gradient-Index Optics and Miniature Optics, (8 April 1988); doi: 10.1117/12.946906

**SPIE.**

Event: 1988 Technical Symposium on Optics, Electro-Optics, and Sensors, 1988, Orlando, FL, United States

## Recent Progress in Gradient-Index Optics

Susan Houde-Walter

The Institute of Optics, University of Rochester  
Rochester, NY 14627

### ABSTRACT

A brief summary of gradient-index (GRIN) optical principles is given, followed by a state-of-the-art review. Much of the important recent work has been in the area of GRIN materials, specifically: new glasses for ion exchange, new ion exchange techniques, GRIN sol-gel glasses and plastic GRIN. New metrology techniques and fabricated GRIN imaging systems are also discussed.

### 1. PRINCIPLES OF GRIN IMAGING OPTICS

Optical materials which contain a distribution of refractive index and are used in lens design are called gradient-index (GRIN) materials. The parameters that define the index distribution provide valuable new degrees of freedom for designers of optical imaging systems<sup>1,2</sup>.

The index distribution can be represented in its most general form by an index polynomial<sup>3</sup>,

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

where  $z$  is the coordinate along the optical axis and  $r$  is the radial coordinate. Two special cases of the general expression for the index polynomial have proven to be particularly useful in lens design. The first of these, called an axial GRIN, is represented by equation (1) by eliminating all terms which include  $r$ . As can be seen from the left hand side of Figure 1, the iso-indicial surfaces are planes, and the index is a function of the coordinate along the optical axis only. 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 (as opposed to a local change in curvature). Figure 2 schematically illustrates the correction of spherical aberration using an axial GRIN profile. Axial GRIN profiles have

been used to correct spherical aberration of collimators<sup>4,5</sup>, binocular objectives<sup>6</sup> and distortion in eyepieces<sup>7</sup>.

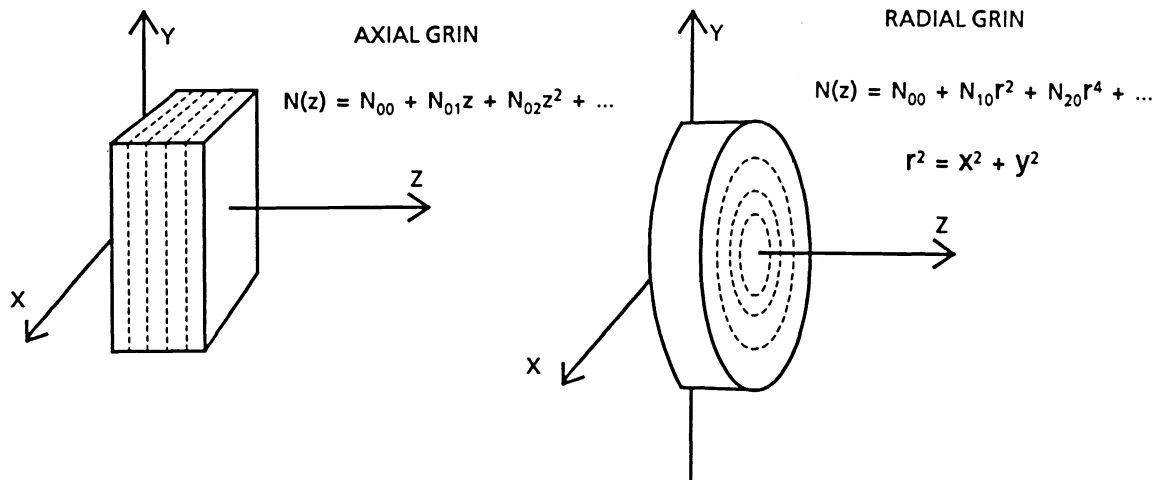


Figure 1. Axial GRIN profile geometry (left) and radial GRIN profile geometry (Right).

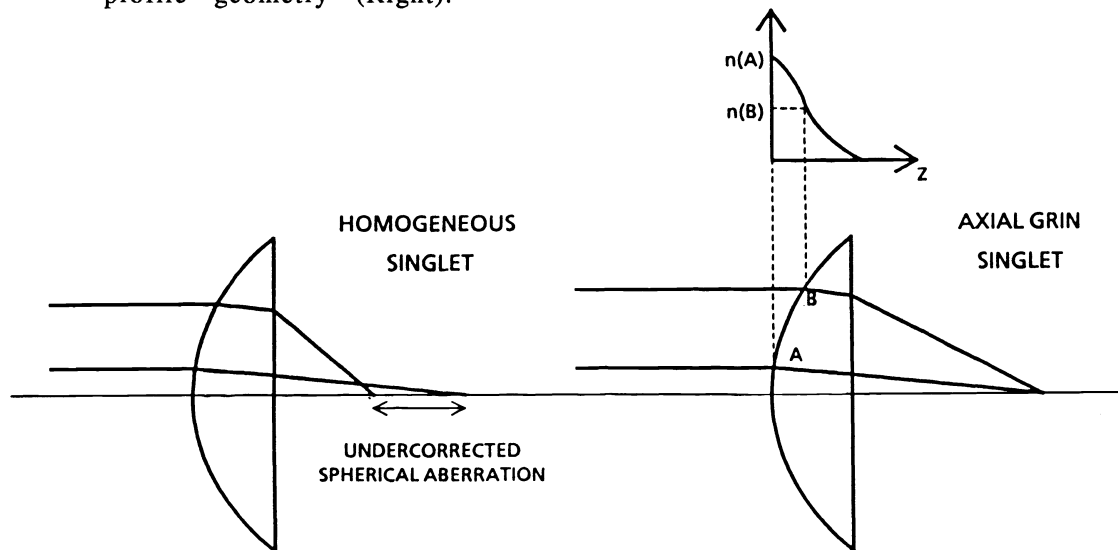


Figure 2. Spherical aberration in a homogeneous singlet with spherical surfaces (left). Correction of spherical aberration using an axial GRIN profile (right).

The second type is the radial GRIN profile, shown on the right hand side of Figure 1. This representation is obtained by eliminating all terms in equation (1) which include  $z$ . Its representation simplifies to the following expression:

$$N(r) = N_{00} + N_{10}r^2 + N_{20}r^4 + \dots \quad (2)$$

The isoindicial surfaces of the radial GRIN are concentric cylinders about the optical axis. Radial GRIN lenses that have plano surfaces are known as Wood lenses, after R.W. Wood who invented them in 1905<sup>8</sup>.

Several interesting features of radial GRIN design can be associated with individual coefficients in equation (2):

1.) The index of the "base" glass is given by the constant term,  $N_{00}$ ; it is the index that one specifies in a homogenous design.

2.)  $N_{10}$  is the coefficient of the quadratic term. This term has the most important consequences for GRIN optics. The power of a thin Wood lens is given by:

$$\Phi_{\text{grad}} = -2N_{10}t \quad (3)$$

where  $\Phi_{\text{grad}}$  is the power due to the GRIN profile and  $t$  is the thickness of the element. This power gives the designer two new degrees of freedom in controlling first-order properties:  $N_{10}$  and element thickness,  $t$ .

Because the GRIN profile has its own optical power, it is effective at correcting aberrations that depend on optical power. Petzval field curvature is a case in point. The contribution to Petzval field curvature due to the presence of the gradient is given by

$$\sigma_{4\text{grad}} = \frac{\Phi_{\text{grad}}}{(N_{00})^2} = \frac{-2N_{10}t}{(N_{00})^2} \quad (4)$$

in analogy with the contribution due to the surface curvatures in homogeneous design. Note that this contribution is inversely proportional to the square of  $N_{00}$ . By using the GRIN profile to increase the power of an element, the designer incorporates less Petzval field curvature than by using the equivalent surface curvatures.

3.)  $N_{20}$  is the fourth power coefficient. It has no effect on power or Petzval field curvature. It can be used to correct other aberrations without changing previously corrected Petzval field curvature or first-order properties. In this way spherical aberration can be decoupled from Petzval field curvature, etc..

The conditions for zero paraxial axial color (PAC) in a GRIN system are derived in a paper by McLaughlin, et al<sup>9</sup>. The derivation is reproduced below.

The total paraxial axial color of a lens composed of thin lens elements in air is

$$PAC_{total} = \frac{1}{u_{ak}^2} \sum_i^{all\ elements} y_{ai}^2 (\Delta\phi_{surf} + \Delta\phi_{grad}) \quad (5)$$

where  $y_a$  is the height of the axial ray, and  $u_{ak}$  is its final angle.  $\Delta\phi_{surf}$  is the difference in power of the surfaces due to the wavelength dependence of the base index. This can be shown to be

$$\Delta\phi_{surf} = \frac{\phi_{surf}}{V} \quad (6)$$

where  $V$  is the Abbe number of dispersion:

$$V = \frac{N_{00d} - 1}{N_{00F} - N_{00C}} \quad (7)$$

Here  $N_{00d}$ ,  $N_{00F}$  and  $N_{00C}$  represent the base indices at yellow, blue and red light respectively.  $\Delta\phi_{grad}$  is the difference in power of the GRIN profile due to the wavelength dependence of the coefficients in equation (8). In the case of a radial GRIN profile, it is given by differentiating equation (3):

$$\Delta\phi_{grad} = -2 (N_{10F} - N_{10C}) t \quad (8)$$

By defining a measure of dispersion for each coefficient in equation (2) in analogy to equation (7),

$$V_{j0} = \frac{N_{j0d}}{(N_{j0F} - N_{j0C})} \quad (9)$$

and  $\Delta\phi_{grad}$  can be written

$$\Delta\phi_{grad} = \frac{\phi_{grad}}{V_{10}} \quad (10)$$

The total PAC for a radial GRIN thin lens singlet will be eliminated if

$$\frac{\phi_{surf}}{V} = \frac{-\phi_{grad}}{V_{10}} \quad (11)$$

The procedure is the same when more than one separate element is present, but the change in axial ray height must be included in the calculations.

Radial GRIN lenses have been used in design studies for color and Petzval field curvature correction in binocular<sup>9</sup> and camera objectives<sup>10</sup>. The

inclusion of radial GRIN in an optical imaging system generally allows the designer to reduce the number of elements by a factor of three while maintaining system performance. Figures 3 and 4 illustrate this point. Figure 3 is a layout of the new double Gauss camera objective reported by Mandler in 1980. This is a high-quality camera objective, compatible with 35-mm film format, operating at  $f/2$  with a focal length of 50 mm and a half-field of view (HFOV) of  $21.8^\circ$ . This objective was redesigned using two elements, each with a common, nearly parabolic index profile. The layout of the GRIN camera objective and a schematic of the index profile are shown in Figure 4. The GRIN design has essentially equivalent performance to the homogeneous design by Mandler.

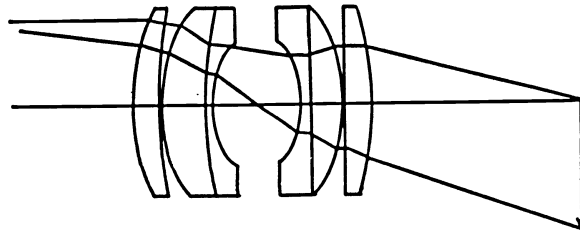


Figure 3. New Double Gauss camera objective. Focal length = 50 mm,  $f/2$ , hfov =  $21^\circ$ . From reference 10.

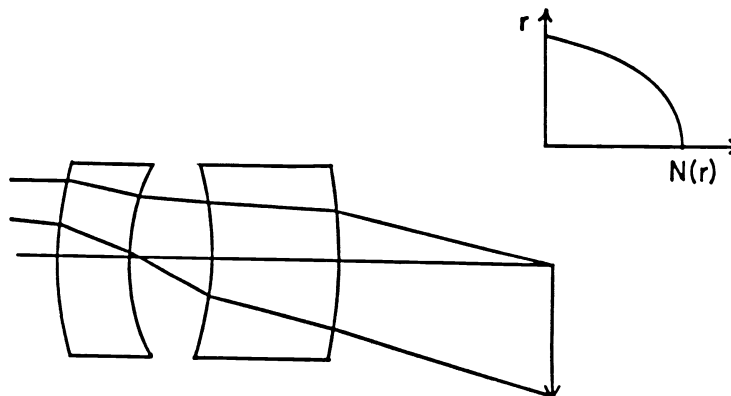


Figure 4. Equivalent radial GRIN camera objective. Focal length = 50 mm,  $f/2$ , hfov =  $21^\circ$ . From reference 10.

Radial GRIN lenses are also used as focusing elements in small geometries. These are usually called GRIN or Selfoc<sup>(R)</sup> rods. Selfoc<sup>(R)</sup> rods have been available commercially for several years from the Nippon Sheet Glass Company (NSG) in Japan, and are now distributed in the United States through

a number of vendors. These have been used for coupling and multiplexing in telecommunications applications (the reader is referred to paper 935-05 of this session by W.J. Tomlinson) and as relay lenses in endoscopes (the reader is referred to paper 935-03 of this session by D.C. Leiner).

Radial GRIN focusing rods are used in strip arrays for commercial desktop copiers (the reader is referred to paper 935-02 of this session by J.D. Rees). The idea here is that each lens has very short conjugates so that the entire system length is on the order of a centimeter. Each lens images a small fraction of the field. The image from each lens overlaps with those of adjacent lenses in a superposition image. Although the total scanned field is large, each lens element has a small aperture and conjugate distances, and needs to be corrected for a small field and aperture only.

A different index representation than equation (2) is commonly used for GRIN rods, although either are equally valid. The GRIN rod index profile is written in terms of the refractive index squared:

$$n^2(r) = n_0^2 \left\{ 1 - (gr)^2 + h_4(gr)^4 + h_6(gr)^6 + \dots \right\} \quad (12)$$

where  $g$  is a constant, referred to as the focusing factor, and the  $h$ 's are additional constants used to describe the index distribution. C.B. Wooley gives an approximate conversion the index polynomial coefficients and the index squared polynomial assuming eighth order expansions as detailed below<sup>11</sup>:

$$\begin{aligned} N_{00} &= n_0 \\ N_{10} &= -\frac{n_0 g^2}{2} \\ N_{20} &= \frac{n_0^2 h_4 g^4 - N_{10}^2}{2 n_0} \\ N_{30} &= \frac{h_6 g^6 - 2 N_{10} N_{20}}{2 n_0} \\ N_{40} &= \frac{h_8 g^8 - 2 N_{10} N_{30} - N_{20}^2}{2 n_0} \end{aligned} \quad (13)$$

Spherical GRIN profiles are index profiles with spherical isoindical surfaces. They are sometimes used in micro-optics applications. The planar microlens array, developed at the Tokyo Institute of Technology, is an example of spherical GRIN profiles<sup>12</sup>. These are made as hemispherical lenslets embedded in a substrate glass (see discussion of field-assisted ion exchange in section 3.2). They are used singly or sandwiched together to form a spherical lens (see Figure 5). Multiple stacks of these lens arrays in combination with

filters, modulators, etc. have been proposed for fiber optic coupling and integrated optics applications. Chapter 10 of reference 13 gives a review of the proposed technology. Figure 6 is a schematic of one such stacked array.

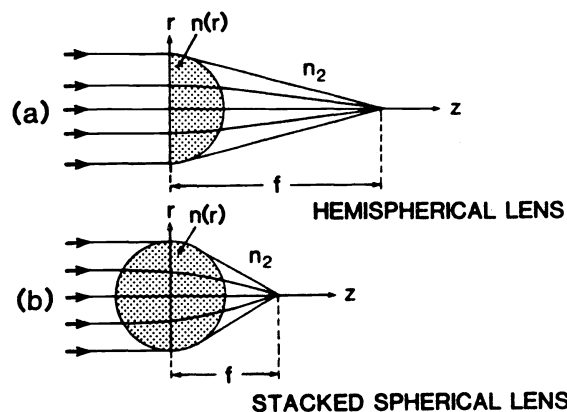


Figure 5. Planar microlenses: hemispherical (top) and stacked spherical (bottom). From reference 12.

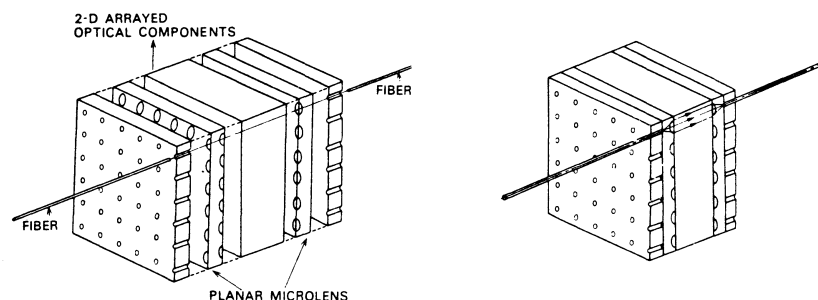


Figure 6. Assembly of stacked planar optics using two microlens arrays for fiber coupling. From reference 13.

## 2. REQUIRED GRIN PARAMETERS

There are three basic parameters to be controlled in the manufacture of GRIN lens blanks. The first is the maximum attainable refractive index difference ( $\Delta n$ ). The  $\Delta n$  determines the focal length in any radial GRIN lens that contains a non-zero quadratic coefficient. Therefore, in order to make fast lenses, large  $\Delta n$ 's are required. For positive lenses, which are the most common type, the refractive index is highest in the center and decreases towards the edge.

The largest fabricated negative  $\Delta n$  has been reported in the patent literature in a patent assigned to Nippon Sheet Glass (U.S. Patent #4,462,663) <sup>14</sup>.

The inventors reported a fabricated  $\Delta n$  of -0.13 by ion exchange in glass. Such large negative  $\Delta n$ 's are possible by melting a very high index homogeneous glass containing thallium. The univalent thallium cation can then be exchanged with another univalent cation, such as potassium, at an elevated temperature. The large difference in polarizabilities of the exchanging ions gives rise to a corresponding change in refractive index. Unless the ion exchange is taken to equilibrium, a larger concentration of thallium will remain in the lens center, while most of the incoming cation will be found near the glass surface. Figure 7 illustrates this point. As a result, the refractive index will be lowered at the glass surface.

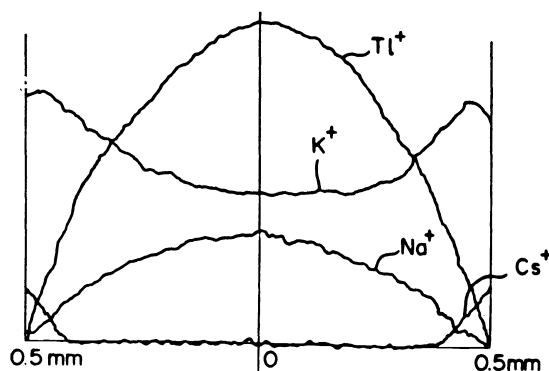


Figure 7. Concentration profiles of index modifier elements in a radial GRIN rod. From reference 14.

Positive  $\Delta n$ 's are also desirable for GRIN imaging systems. Misawa, et al, reported the largest positive  $\Delta n$  to date. This was accomplished by diffusing thallium into Schott TiF6 optical glass. The resulting  $\Delta n$  was 0.27<sup>12</sup>. Although the resulting glass is somewhat brittle, it has excellent optical transparency.

Large radial and axial GRIN imaging systems designs are commonly constrained to  $\Delta n$ 's no greater than 0.10. Bigger  $\Delta n$ 's may be useful, but they are usually held to this limit because it is thought to be the largest value that can be routinely fabricated in large geometries.

Many GRIN lens designs also require large profile depths. The profile depth is equal to the radius of a radial GRIN lens. In order to make radial GRIN objective lens designs, profile depths must sometimes reach tens of millimeters<sup>9,10</sup>. An alternative approach is to find applications for which small radial GRIN elements are useful. The Selfoc(R) rod lens is one example of this philosophy.

In axial GRIN lenses, the profile depth determines the maximum allowable sag of the lens surface. In this case the required depths are smaller, generally on the order of a few millimeters.

The shape of the index profile is also important to the GRIN lens designer<sup>5</sup>. Linear index profiles have been shown to be useful in axial GRIN collimators<sup>4</sup>. Parabolic profiles are used in focusing rods<sup>14</sup>. More general index profile types are useful in well-corrected multi-element designs with conventional specifications<sup>10</sup>.

The above specifications mandate new materials in order to fabricate GRIN lens designs. As recently as three years ago, the number of GRIN lens designs that had been fabricated was limited to the axial GRIN collimator<sup>4</sup> the microlens arrays<sup>12</sup> and those designs which incorporated the Selfoc(R) rods. Lately, both the fabrication and testing technologies have advanced to the point where new designs are being fabricated. The remainder of this paper reviews these recent advances.

### 3. GRIN MATERIALS

#### 3.1 Ion Exchange in Glass

The most common method for fabricating GRIN materials is cationic diffusion from a molten salt into a batch-melted (or "base") glass. The base glass can be thought of as containing three categories of oxide components. The glass formers, the intermediates, and the glass modifiers. The formers determine the basic molecular structure of the glass and can form glasses by themselves. Examples of glass formers are silica ( $\text{SiO}_2$ ), phosphorous pentoxide ( $\text{P}_2\text{O}_5$ ), germanium dioxide ( $\text{GeO}_2$ ) and boron oxide ( $\text{B}_2\text{O}_3$ ). The intermediates also contribute to the structure of the glass, but cannot be made into glasses by themselves. Alumina ( $\text{Al}_2\text{O}_3$ ), lead oxide ( $\text{PbO}$ ) and zincite ( $\text{ZnO}$ ) are examples of glass intermediates. The network modifiers are weakly bound to the other glass components by non-bridging oxygens and so have little effect on the glass structure. These include the alkali oxides, e.g. soda ( $\text{Na}_2\text{O}$ ), potash ( $\text{K}_2\text{O}$ ) and lithia ( $\text{Li}_2\text{O}$ ), and many other oxides such as lime ( $\text{CaO}$ ), barium oxide ( $\text{BaO}$ ), cesium oxide ( $\text{Cs}_2\text{O}$ ) and rubidium monoxide ( $\text{Rb}_2\text{O}$ ), etc. A complete table of glass components and their classifications can be found in reference<sup>15</sup>.

The basic picture of the structure of oxide glasses is the random network model. In this model the glass formers and intermediates are arranged in a loosely ordered network (see Figure 8). The former-intermediate network is thought to be fixed and rigid below the softening point, with the modifiers migrating from site to site, exchanging amongst themselves at rates determined by the glass structure and temperature. 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.

Most commercial optical glasses are oxide glasses (the fluoride glasses being the exception). These glasses typically have seven to ten components, except for some of the heavy flint glasses which have fewer components. The composition and thermal history of optical glasses have been optimized for index of refraction, dispersion, homogeneity, strength, and, if possible,

chemical durability. As a consequence, commercial optical glasses generally have poor transport properties.

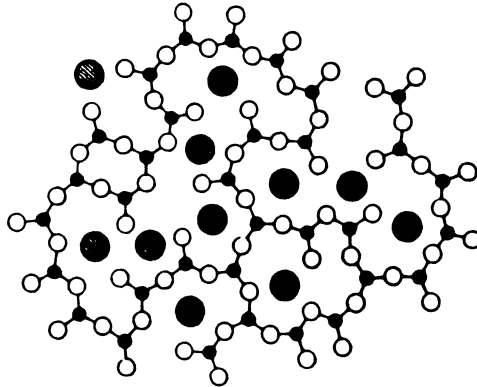


Figure 8. Two dimensional sodium silicate glass structure. Open circles represent oxygen, small closed circles represent silicon, large closed circles represent sodium. From reference 15.

The rate of transport of an ion in an isotropic medium such as glass depends on the ionic mobility of the incoming species as measured in that glass. In general, the mobility of the incoming ion is different than that of the indigenous ion.

Interdiffusion in the absence of an externally applied field is governed by the diffusion equation<sup>16</sup> and is written in one dimension by equation (14),

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x} \left\{ D(C) \frac{\delta C}{\delta x} \right\} \quad (14)$$

where  $C$  is the concentration of the dopant in moles,  $D(C)$  is the interdiffusion coefficient and  $x$  and  $t$  are space and time variables, respectively. The functional form of the interdiffusion coefficient can be derived from basic principles as<sup>17</sup>:

$$D(C) = \frac{D_{in}}{1 - \alpha C/C_0} \quad \text{where } \alpha = 1 - \frac{D_{in}}{D_{out}} \quad (15)$$

$D_{in}$  is the self-diffusion coefficient of the incoming (dopant) ion,  $D_{out}$  is that of the out-going ion, and  $C_0$  is the concentration of the out-going ion before diffusion begins.

The functional form of the solution to the diffusion equation depends on the ratio of the mobilities of the incoming and constituent ions and also on the boundary conditions. One of the simplest examples is the diffusion from an undepletable source, such as a large molten salt bath, into a semi-infinite slab of glass which contains no dopant before the diffusion begins. In the special

case that the ionic mobilities are equal, the resulting concentration profile is given by,

$$C(x,t) = C_0 \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} \right\} \quad (16)$$

where  $D_{in} = D_{out} = D$  and  $\operatorname{erfc}$ , the complementary error function, is given by

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-\eta^2} d\eta \quad (17)$$

The more general case of unequal ionic mobilities has been solved by Fujita<sup>16</sup>. The solutions are plotted in Figure 9. The parameter "M" is the ratio of the mobilities of the dopant to the indigenous ion. As can be seen from the figure, when the dopant ion is less mobile in the host than the glass constituent ion, little mixing occurs and the concentration profile is steep. As the mobilities become more nearly equal, the degree of mixing increases and the resultant profile shape is less abrupt. The  $\operatorname{erfc}$  solution for equal mobilities is shown for comparison ( $M=1$ ).

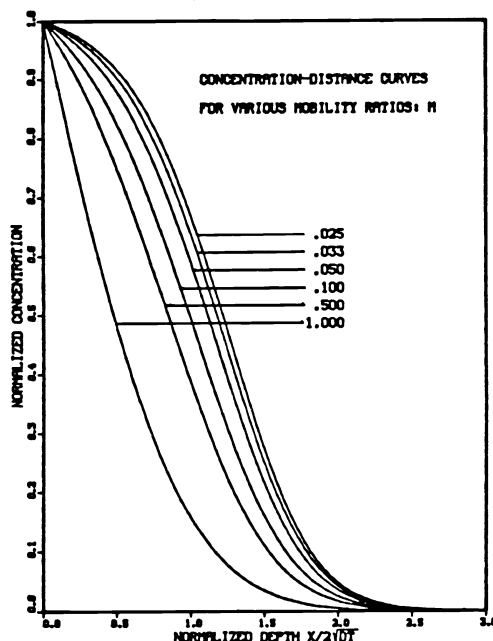


Figure 9. Normalized concentration profiles for various mobility ratios,  $M$ , versus normalized diffusion depth,  $x/2(D_{int})^{1/2}$ .

In practice, the concentration dependence of the interdiffusion coefficient is obtained from the concentration profile using the Boltzmann-Matano method<sup>16</sup>. The applicability of equation (15) is fairly limited. Many other

types of concentration dependence have been observed experimentally, including exponential dependences<sup>18</sup>.

### 3.2 Field-Assisted Ion Exchange

Field-assisted ion exchange can be used to extend the repertoire of profile shapes and to speed the ion exchange process for GRIN applications<sup>19</sup>. For systems with equal ionic mobility, the one-dimensional diffusion equation becomes:

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} - \mu E \frac{\delta C}{\delta x} \quad (18)$$

Here E is the applied field strength and  $\mu$  is the common ionic mobility. The resulting concentration profile for constant boundary conditions is:

$$C(x,t) = \frac{1}{2} C_0 \left\{ e^{\mu E x / D} \operatorname{erfc} \left\{ \frac{x + \mu E t}{2\sqrt{Dt}} \right\} + \operatorname{erfc} \left\{ \frac{x - \mu E t}{2\sqrt{Dt}} \right\} \right\} \quad (19)$$

This profile is shown in Figure 10. The profile is given for a forward field application (driving dopant into the glass), a forward and then reversed field (ion is driven in and then out of glass), and finally a field application where the polarity is changed twice. Families of profile types suitable for GRIN applications have recently been published<sup>19</sup>.

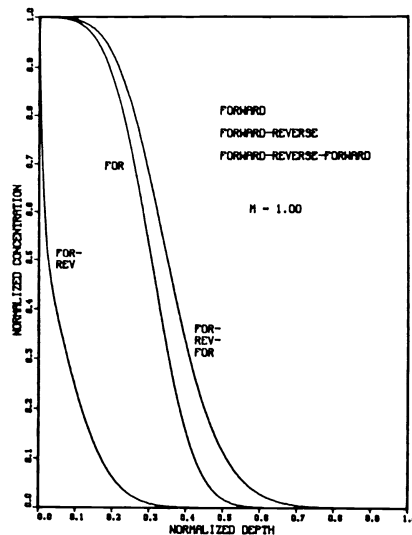


Figure 10. Normalized concentration versus normalized depth for a forward, forward-reverse, and a forward-reverse-forward field application. Equation (19) corresponds to the forward field application. From reference 19.

Field-assisted ion exchange has also been used to produce arrays of small embedded hemispherical lenslets<sup>20</sup>. The substrate glass is coated on one side with a mask that has an array of pinholes. The pinholes are about 100 microns in diameter. An external field is applied which drives the dopant into the glass through the pinholes. (See Figure 11). The result is small, nearly perfectly spherical GRIN profiles.

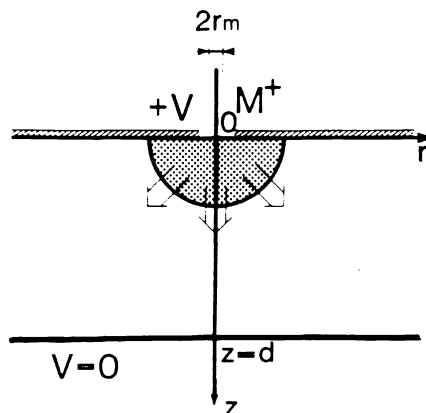


Figure 11. Field-assisted ion exchange through a small circular hole of radius  $r_m$  into a glass slab of thickness  $d$ . Resulting isoindicial surfaces are nearly perfect concentric hemispheres. From reference 20.

### 3.3 New Metrology Methods

In ion exchanged glass, the boundary conditions, concentration dependence of the glass/salt pair and structural changes during diffusion all determine the final index profile. In theory, a detailed knowledge of these parameters is necessary to predict the final index profile from the diffusion equation. In practice, they are not well understood.

Recently an interferometer was reported that measures the index profiles in GRIN glass as they are forming by ion exchange<sup>21</sup>. The instrument is an a.c. Mach-Zehnder with a diffusion oven in the test arm. For the first time, the evolution of index profiles were monitored during normal diffusion conditions, annealing conditions and under rate-limited boundary conditions. The instrument is expected to be useful in the study of new salt melt and glasses for ion exchanged GRIN glass. Figure 12 demonstrates one such measurement. Here one can see the index profile form at 1/2 hour intervals<sup>22</sup>. It is clear that the dopant transport occurs at a finite rate across the glass/salt interface. This rate will determine the maximum obtainable  $\Delta n$  for a given diffusion time and temperature.

### 3.4 New Base Glasses for GRIN ion exchange

One of the facts of life that every lens designer must contend with is that there is a finite number of available optical glasses. Thus, in the early stages of a lens design, the designer often comes up with a lens made from a hypothetical glass that does not have the same specifications as any available glass. The designer must identify a real glass close in specification to the ideal glass, and redesign the system. This is generally a compromise that one can live with since there are a large number of available optical glasses.

The designer of GRIN lens systems faces a severe shortage of usable glasses, on the other hand. The reason is that diffusions are too slow in most commercial optical glasses for the large diffusion depths required in GRIN systems to be practical.

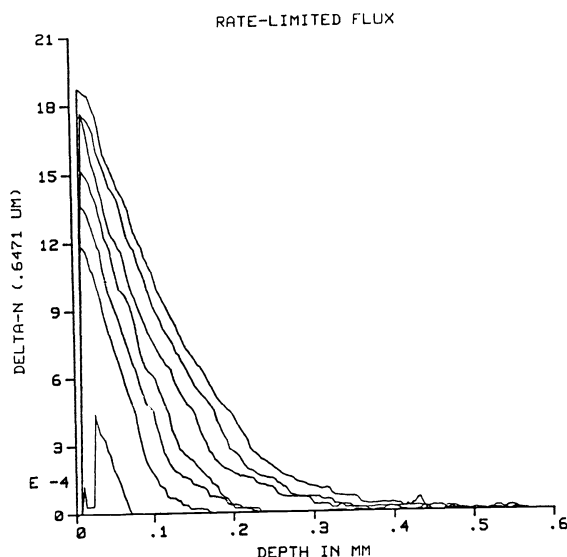


Figure 12. Initial stages of an axial GRIN profile formation at 490°C. Profiles are shown at 1/2 hour intervals. Measurement by oven interferometer. From reference 22.

Much of the reduction in diffusion rates can be attributed to the mixed alkali effect. This effect gets its name because when a glass contains more than one alkali oxide, several glass properties, e.g. ionic mobility, depend on the relative mole fraction of each alkali component in a highly non-linear fashion. One of the important consequences for making GRIN glass is the fact that diffusion rates in mixed alkali glasses are often one or more orders of magnitude slower than in their single alkali counterparts.

A second reason for the shortage of good GRIN base glasses can be found in the valence of the glass modifier constituents. Univalent cations in a single alkali glass are the most mobile, with diffusion coefficients often on the order of  $10^{-8} \text{ cm}^2\text{s}^{-1}$ . Bivalent cations, however, move much more slowly in the glass matrix and have much smaller diffusion coefficients, sometimes two orders of magnitude slower, other conditions being equal. Commercial optical

glasses which fall along the glass line typically contain univalent cations. These glasses would include the BK, K, LLF, LF F, TiF and SF groups, if one refers to the Schott glass catalog. However, it is often advantageous to use a base glass that resides away from the glass line. This is commonly required for reduction of color aberrations, etc.. The requisite glasses have a high refractive index, yet a low dispersion, e.g. the LaK glasses. These glasses do not contain univalent modifiers for ion exchange however. It is clear from previous lens design studies (see reference 10) that high index/low dispersion base glasses would be very useful for GRIN optics.

Some interesting new GRIN base glasses have recently been designed by Kindred which promise to improve this situation<sup>23</sup>. Kindred points out that while many diffusions have been conducted in various optical glasses<sup>24,25</sup>, only a few of these result in  $\Delta n$ 's larger than 0.02. Such small  $\Delta n$ 's leave the designer with little flexibility in engineering index profiles.

Kindred has recently developed three new glass families. The first is a series of titania flint glasses for diffusion with lithium salts. These flints were made in both ternary and quaternary systems. The first flint groups are Na<sub>2</sub>O-TiO<sub>2</sub>-SiO<sub>2</sub> ternaries. Using 25 mole percent soda and less than 20 mole percent titania gives resistance to devitrification and cracking when exchanging Li<sup>+</sup> for Na<sup>+</sup>. Both the  $\Delta n$  and the base refractive index increased with TiO<sub>2</sub> concentration, as one might expect, since the alkali fraction was fixed. The highest index glass in this group (0.20 TiO<sub>2</sub>) has a base index of 1.637 at 0.6328 microns, and yields a  $\Delta n$  of 0.05 at the same wavelength when exchanged from a LiCl/CaCl melt. The Abbe dispersion number of this glass is 32 and the gradient dispersion number is 27.

Titania flint quaternaries were also investigated. These glasses are stronger than their high-soda counterparts. Although they are mixed alkali glasses, diffusion depths on the order of 3 mm are achievable by diffusing Li<sup>+</sup> from LiCl/CaCl melts at 550°C for 72 hours. Figure 13 shows the index profiles in three of these glasses with various ratios of soda and lithia mole fractions. As can be seen from the figure, glasses with a larger mole fraction of soda impart a larger  $\Delta n$  when diffused with Li<sup>+</sup>. This, of course, is because the second alkali component is lithia, so that any Li<sup>+</sup> diffusion that involves the lithium glass component will not result in a change in refractive index. The resulting index profiles are dominated by the linear term in the index polynomial. They should therefore be useful for designs requiring linear index profiles.

The two remaining glass families recently developed by Kindred are glasses with large negative  $\Delta n$ 's. A crown glass with a base index greater than 1.6 and an Abbe number of about 57 gives  $\Delta n$ 's on the order of -0.06. The gradient dispersion is large, however. In applications where this dispersion can be tolerated, this glass should be useful for powerful radial GRIN rod lenses. The last family falls in the BK and K ranges of the Schott glass map. The  $\Delta n$ 's are smaller (approximately -0.01) but the gradient dispersion is low. These may be useful for slow achromatic Wood lenses. Both glass families should be useful in expanding the repertoire of glasses useful in multicomponent GRIN optical systems, as should the aforementioned flints.

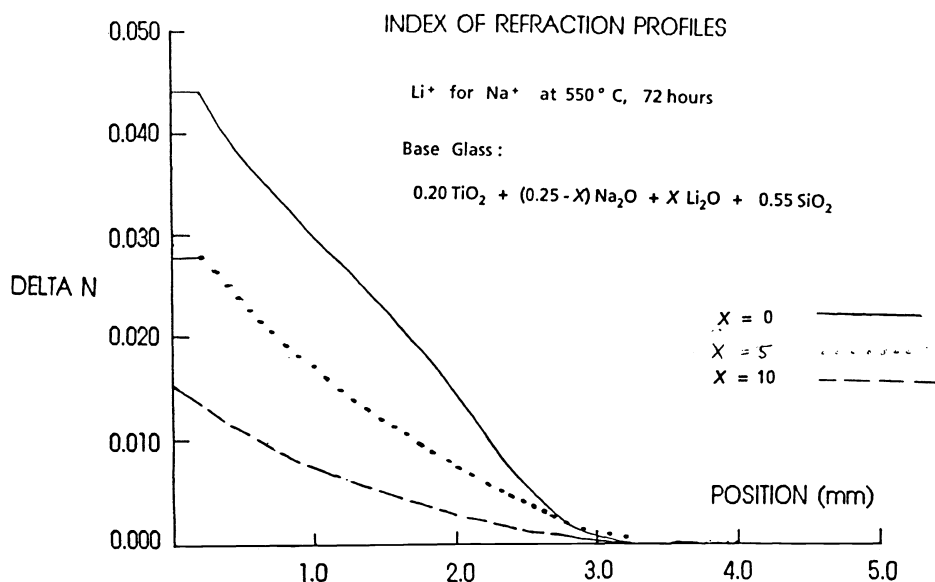


Figure 13. Diffused index profiles in three titania silicate glasses.  
From reference 23.

### 3.5 Ion-stuffed GRIN glass

Ion exchanged thallium glasses have been widely used for fabricating radial GRIN rods. Thallium glasses have many advantages, including excellent optical transparency, but they suffer from two major drawbacks. The first is the very high toxicity of thallium. This is particularly dangerous in the glass-melting stage where the vapor pressures are high. The second is the relatively low mobility of  $Tl^+$  as compared to the alkali ions.

Silver is sometimes used as an alternative to thallium because it has a higher mobility, often by an order of magnitude. It is difficult to make silver glasses from a batch melt, however, because the silver tends to precipitate out of the glass or form a fine metallic colloid in the glass<sup>26</sup>. The resulting glass composition is silver-poor compared to the batch formula, and may be colored due to the metal colloid.

A new technique called "ion-stuffing" avoids the difficulty of making silver glass from a batch melt<sup>27</sup>. The idea is to take a soda-containing glass and exchange the  $Na^+$  for  $Ag^+$  to equilibrium ("stuffing"). The result is a homogenous silver glass. The second step is to immerse the silver glass in a  $Na^+$  containing melt and exchange some of the  $Ag^+$  out near the surface of the glass ("unstuffing"). The final glass has a high concentration of silver (and hence a higher index of refraction) than the surface which is silver-poor. Ohmi, et al, have made 2.0 and 9.4 mm diameter radial GRIN rods in this manner. The first of these had a  $\Delta n$  of approximately 0.06 and a numerical aperture of 0.57.

This author would expect that it is important to conduct the diffusions at temperatures well below the glass transition temperature so that formation of a metallic colloid is not encouraged. Ohmi and his collaborators conducted the diffusions from nitrate melts at 400 and 430°C, which is below most silicate glass transition temperatures. The stuffing took 62 hour in a 2 mm diam rod, and the unstuffing took less than 7 hours. Not all of the Na<sup>+</sup> is replaced by silver in the stuffing step. Perhaps this is why such a large mole fraction of soda (0.40) is included in the starting glass composition.

### 3.6 Sol-Gel GRIN Glass

The sol-gel method is a new technique for fabricating GRIN glass. The method involves the synthesis of a multi-component alkoxide gel, which is shaped by a mold. The gel is porous, so dopants can be introduced (or removed) rapidly by immersing the gel in a solution containing dopants (or acids for leaching). The doped (leached) gel is then dried and consolidated to form a clear GRIN glass. The method has two major advantages over ion exchange in glass: 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 are easily transported through the gel pores.

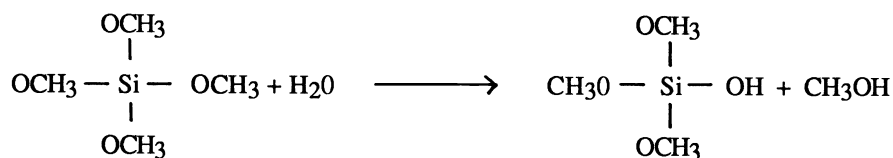
An alkoxide is similar to an alcohol. An alcohol has the formation ROH where R is an alkyl group, for example: R = CH<sub>3</sub> (methyl), R = C<sub>2</sub>H<sub>5</sub> (ethyl), R = C<sub>3</sub>H<sub>7</sub> (propyl), etc. A metal alkoxide has the general formula M(OR) where M is a metal. Thus, the metal has replaced the H in the ROH alcohol formula. Two common alkoxides are:

Si(OCH<sub>3</sub>)<sub>4</sub> - Tetramethoxysilane or "TMOS"  
Na(OCH<sub>3</sub>) - Sodium methoxide

The chemistry of a simple sol-gel process to make SiO<sub>2</sub> is shown in Figure 14. TMOS (the metal alkoxide) is mixed with water and a solvent to form an oxide gel. In the first step hydrolysis of the TMOS gives rise to an intermediate and methyl alcohol. In the second step, two intermediates form a Si-O-Si bond, giving off water as a by product. This process continues until a wet, porous gel is formed. It is into this wet gel that ion exchange or leaching is done.

One of the first reports of using sol-gels for making GRIN glass appeared in a patent by M. Yamane (U.S. Patent Serial No. 820,486). According to this patent, by combining a silicon alkoxide with water, some source of boron oxide and an aqueous metal salt solution, a gel could be formed in a mold. The gel is then immersed in a solution containing another species of metal salts which exchange with the constituent metal salts. After the diffusion, the gel is dried and sintered to yield a GRIN glass. The index profiles were difficult to control, however, because the salts continued to migrate during the drying process.

#### HYDROLYSIS:



#### CONDENSATION:

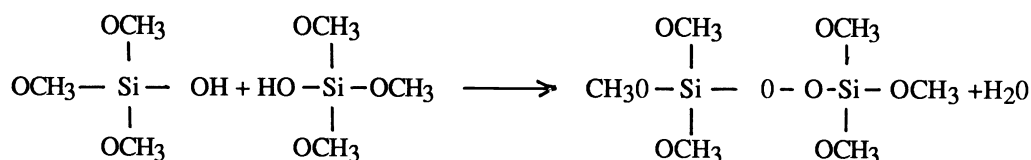


Figure 14. The two steps of sol-gel formation as illustrated by a simple silicate glass. Step 1: hydration; step 2: condensation.

A similar implementation of this method was recently reported by Yamane, et al<sup>28</sup>. In this report,  $\text{Pb}^{++}$  ions were exchanged with  $\text{K}^+$  ions in the gel diffusion stage, an exchange that cannot be utilized in conventional diffusion in glass. A 6 mm diameter radial GRIN rod with a  $\Delta n$  of 0.016 was produced.

Shingyouchi, et al overcame this problem by binding the index modifier to the gel structure<sup>29,30</sup>. This was done by doping the gel with an alkoxide of germanium, rather than a salt. As reported by Shingyouchi and his colleagues, tetramethoxygermanium, TMOS, ethanol, water and hydrochloric acid are combined to form the gel. Once formed, the gel is immersed in water to partially leach out the germanium component. The distribution is then fixed by immersion in methanol. After drying, the gel is sintered into GRIN glass. The final radial GRIN rods had a diameter of over 3 mm, a nearly parabolic distribution and a  $\Delta n$  of approximately 0.025 (numerical aperture of 0.27). This technique was later generalized to incorporate titanium or zirconium in place of germanium. The resulting germanium GRIN rod had a 2 mm diameter with a  $\Delta n$  of -0.013.

The sol-gel method as described above is beautifully simple. Improvements can be made to the resulting GRIN glass if some modifications to the method are made, however. The above binary gels suffer appreciable shrinkage during the gel-drying step. The resulting dense gel consolidates more quickly on the edges during sintering, trapping gaseous by-products inside. The gels are also prone to fracture during sintering, and the  $\text{SiO}_2/\text{TiO}_2$  gel sometime crystallizes if the  $\text{TiO}_2$  content is above 5 mole percent.

These problems can be circumvented by making gels with three or more components. A recent patent application (serial #7/59,906, 1987) by Caldwell and Moore describes the technique. Two or more metal alkoxides are combined with a silicon alkoxide to form the gel. The  $\text{SiO}_2$  component should be between 60 and 90 mole percent for strength. The first metal alkoxide serves as the index modifier. These might be alkoxides of titanium or zirconium. These components should be limited to less than 25 mole percent to maintain gel stability, but large enough to provide a useful change in index. The second metal alkoxide serves as the gel modifier. These might be alkoxides of boron, aluminum or germanium. Gels incorporating alumina have a coarser microstructure after drying than gels without. The coarse structure allows gases to escape during sintering and makes the gel less likely to fracture during drying because they shrink less. The alumina also increases the required sintering temperature. Consequently the reactions which form gaseous by-products are more likely to be completed by the time the gel begins to collapse into a dense glass. Boron and germanium act in a similar manner, except that germanium also contributes to the final  $\Delta n$ .

The alkoxides are combined with methanol, an aqueous solution of hydrochloric acid and water and the mixture is poured into plastic molds. The gel forms in a few hours at room temperature, and are aged at  $60^\circ\text{C}$  for 24 hours. The metal alkoxide components are then partially leached out by immersion in an aqueous solution of sulphuric acid. The leaching is fixed by a methanol wash. The gels are afterwards dried at temperatures near  $100^\circ\text{C}$  for a total of three days. Finally, the gels are sintered in a carefully controlled temperature ramp which peaks at  $1450^\circ\text{C}$ .

Figure 15 shows the index profile at 0.6328 micron of a typical sol-gel GRIN rod. It has a nearly parabolic profile, with a diameter of over 4 mm and a  $\Delta n$  of approximately 0.012. The inner diameter of the original gel mold was 15 mm. Since there does not appear to be any fundamental reason why this technique can't be scaled up, it is considered to be one of the most promising methods for making large diameter radial GRIN rods.

### 3.7 Plastic GRIN

Plastic GRIN materials are an alternative to glass GRIN when lighter weight is necessary and high thermal expansion coefficients are unimportant or are used to athermalize an optical system<sup>31</sup>. There are two prevailing methods. The first is called photocopolymerization and the second is a monomer diffusion process.

Photocopolymerization can be described as follows<sup>32</sup>: a glass tube is filled with a mixture of three monomers and an initiator. The tube is exposed through a slit to a source of ultra-violet light and rotated about its axis. (See Figure 16.) The slit is perpendicular to the tube axis and moves slowly up along its length. The copolymer thickens with exposure and forms first on the inner walls of the tube. At this early stage, the polymer conversion is at the threshold gelation rate. By the time the mixture is completely solidified throughout the tube, the polymer conversion is at a different rate. As the

conversion of the copolymer formed along the inner walls gradually changes to its final value, a radial distribution of copolymer composition is created. Afterwards the rod is cured for 80°C for 24 hours. Many types of index profiles can be made depending on the choice of monomers.

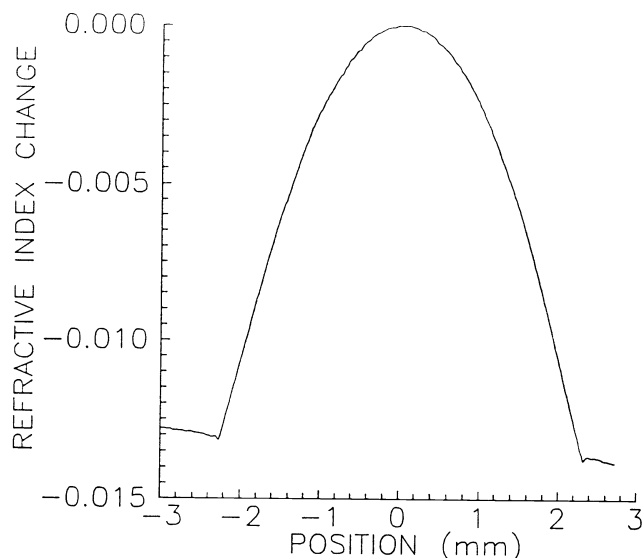


Figure 15. Nearly parabolic radial GRIN profile made by the sol-gel process.

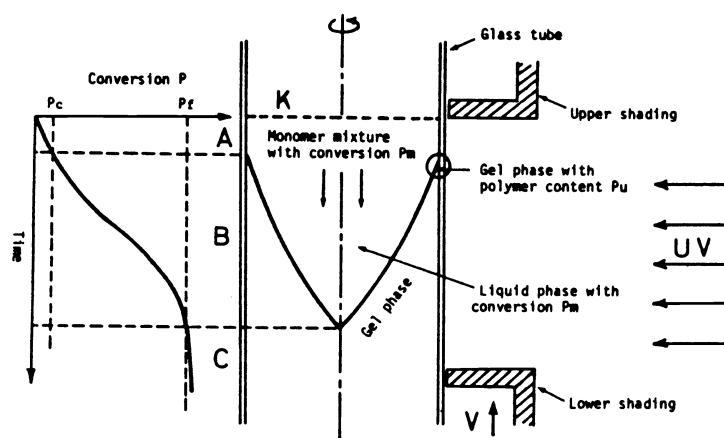


Figure 16. Photocopolymerization of multi-component monomer mixture. From reference 32.

The diffusion process involves pouring a monomer-initiator mixture into a mold and heating to form a partially polymerized rod. The gel is then removed from the mold and placed in a diffusion chamber with a second monomer which diffuses into the gel rod. Afterwards the gel is completely polymerized

by returning it to the mold and heating. Monomers used to date are CR39 (polymer index = 1.50), 3FMA (polymer index = 1.46) and HIRI (polymer index = 1.56)<sup>33</sup>. These may be used in different combinations to produce either positive or negative radial GRIN rods. Plastic GRIN rods with diameters of over 20 mm and positive  $\Delta n$ 's of over 0.03 have been fabricated using this method.

#### 4. NEWLY FABRICATED GRIN SYSTEMS

Three new GRIN optical systems have recently been reported. Two involve the optical disk and the third is a retrofit of the M19 binocular objective. All three were manufactured by ion exchange in glasses.

A plano convex radial GRIN single element objective was fabricated for the compact disk application<sup>34</sup>. The first order properties include a focal length of 3.6 mm, a numerical aperture of 0.45 and a 1.9 mm working distance. The lens had to be diffraction limited at 0.780 microns and the wavefront error (WFE) could not exceed the Marechal criterion (rms WFE cannot deviate by greater than  $0.07\lambda$ ) over the whole field.

Several prototype lenses were fabricated with the following dimensions: 4 mm diameter, a front radius of curvature of 2.7 mm, axial thickness of 1.6 mm and a total mass of approximately 50 milligrams. A nearly parabolic index profile was developed for this work, with a  $\Delta n$  of over 0.08. Fringe patterns from a Fizeau interferometer were reported; they showed that the lens meets the stringent specifications mentioned above. The lenses were used in a prototype compact disk system. A layout of the objective is shown in Figure 17.

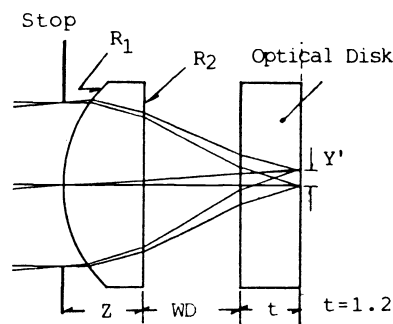


Figure 17. Layout of a radial GRIN objective fabricated for the compact disk. From reference 34.

An axial GRIN with a linear index profile was developed for use in a compact disk collimator<sup>5</sup>. A single element collimator was successfully fabricated to meet the Marechal criterion at 0.780 micron. The lens has 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. The glass type and dopant source were not reported, although the  $\Delta n$  was given as 0.017.

The previous two examples involved small, high performance lenses, where the advantage is in reducing the number of such small lens elements that must be aligned. The last example is in an entirely different regime. The project was to replace the objective of the M-19 binocular<sup>35</sup> with a GRIN objective. This was done using axial GRIN profiles.

The first order specifications of the binocular objective are: focal length of 150 mm,  $f/3$ , HFOV of  $3.7^\circ$ , entrance pupil of 50 mm and a telephoto ratio of 0.80<sup>36</sup>. The original design used three homogeneous lenses with spherical surfaces. The GRIN design used two elements with spherical surfaces. The GRIN profile was in the rear sag of the first element.

A  $\text{Ag}^+$  for  $\text{Na}^+$  ion exchange from a mixed silver chloride melt in a simple aluminosilicate glass was chosen because it was a well characterized diffusion system. The base index of the glass is 1.501 at the sodium d line and it has an Abbe dispersion number of 58. The GRIN dispersion number is approximately 15 when diffused with silver. The maximum  $\Delta n$  was limited to 0.05 in the design because the glass tends to yellow with a higher corresponding silver content.

The GRIN objective was optimized as part of the entire binocular with fixed prisms, field lens and eyepiece as the original system. Although the on-axis performance was good, a modification of the field lens was required to match the performance of the original system off-axis. Once done, the performance of the GRIN retrofit was essentially equivalent to the original system<sup>37</sup>. Spot diagrams of the GRIN design, the GRIN design with the fabricated index profile and the three element homogeneous system design are shown in Figure 18. Comparison of the two objective layouts are shown in Figure 19.

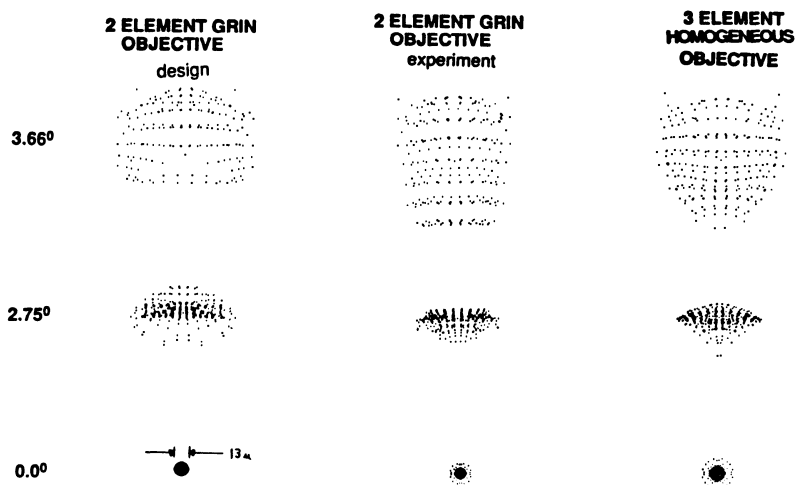


Figure 18. Comparison of spot diagrams of binocular system: GRIN design (left), GRIN design using experimental profile (middle) and three element homogeneous system design (right) From reference 36.

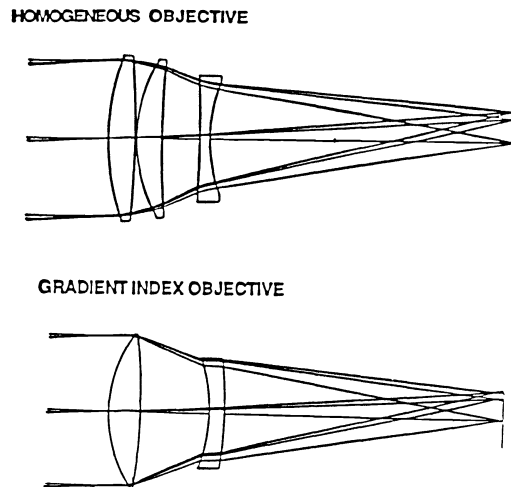


Figure 19. Layouts of the M-19 binocular objective. Top: original three element homogeneous objective, bottom: two element axial GRIN objective. Index profile is in rear of first element.

## 5. SUMMARY

Recent progress in the field of GRIN optical imaging systems has been reviewed. Much of the recent activity has been concentrated in the area of GRIN fabrication. This includes ion exchange techniques, the development of new base glasses for ion exchange, sol-gel GRIN glass and plastic GRIN. Since the benefits of using GRIN parameters are well known, it is reasonable to expect that GRIN parameters will be employed in an increasing number of lens designs as suitable materials become available. Judging from the recent progress in this area, that may occur in the near future.

## 6. ACKNOWLEDGEMENTS

The author would like to acknowledge several interesting discussions with J.B. Caldwell, L. Gardner, D.S. Kindred, M. Oikawa and C.B. Wooley.

## 7. REFERENCES

1. D.T. Moore, "Gradient-Index Optics: A Review," *Appl. Opt.*, v19, p1035 (1980).
2. D.B. Keck, "GRIN V: Progress in Gradient-Index Imaging," *Appl. Opt.*, v.24, p4287 (1985).
3. D.T. Moore, Gradient Index Optics: Aspects of Design, Testing, Tolerancing and Fabrication, Doctoral Thesis, University of Rochester, 1974.
4. D.T. Moore, "Design of Single Element Gradient-Index Collimator," *J. Opt. Soc. Amer.*, v.67, p1137 (1977).
5. P.O. McLaughlin, et al, "Axial gradient index singlet collimator lens for the compact disk system," *Proc. SPIE v.695 Optical Mass Data Storage II* p194-8, San Diego, CA (1986).

6. J.B. Caldwell, et al, "Gradient-Index Binocular Objective Design," Appl. Opt., v.25, p3345 (1986).
7. J.D. Forer, et al, "Gradient-Index Eyepiece Design," Appl. Opt., v.22, p407 (1983).
8. R.W. Wood, Physical Optics, Macmillan, New York, 1905 (p71).
9. P.O. McLaughlin, et al, "Design of a Gradient-Index Binocular Objective," SPIE Proc. of the OSA 1980 International Lens Design Conf., v.237, p369.
10. L.G. Atkinson, et al, "Design of a Gradient-Index Photographic Objective," Appl. Opt., v.21, p993 (1982).
11. C.B. Wooley, unpublished.
12. S. Misawa, et al, "Maximum and effective numerical apertures of a planar microlens," Appl. Opt., v.23, p1784 (1984).
13. K. Iga, Y. Kokubun and M. Oikawa, Fundamentals of Microoptics, Academic Press, New York, 1984.
14. U.S. Patent #4,462,663, "Converging Light Transmitting Body of High Performance and Process for Production Thereof," M. Shimizu, et al, assigned to Nippon Sheet Glass, Osaka, Japan, 1984.
15. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, Introduction to Ceramics, 2nd edition, John Wiley & Sons, New York, 1970.
16. J.R. Crank, The Mathematics of Diffusion, 2nd edition, Oxford University Press, 1975.
17. R.H. Doremus, Glass Science, John Wiley & Sons, New York, 1973.
18. X.F. Zhu, et al, "Change of Index Profile in a Planar Microlens by Ion Exchange/Diffusion," Paper B3, 6th Topical Meeting on Gradient-Index Optical Imaging Systems, Palermo, Italy, 1985.
19. S.N. Houde-Walter and D.T. Moore, "Gradient-Index Profile Control by Field-Assisted Ion Exchnage in Glass," Appl. Opt., v.24, p4326 (1985).
20. M. Oikawa, et al, "Distributed-Index formation process in a planar microlens," Appl. Opt., v.23, p1787 (1984).
21. S.N. Houde-Walter and D.T. Moore, "Real-time index profile measurement during GRIN glass fabrication," Appl. Opt., v.27, p.508 (1988).
22. S.N. Houde-Walter and D.T. Moore, "Development of Concentration at Glass/Salt Interface in Diffusing GRIN Glass," J. Non-Cryst. Sol., v.99, p.104 (1988).
23. D.S. Kindred, D.T. Moore, "Gradient-Index  $\text{SiO}_2\text{-TiO}_2\text{-NaO}_2\text{-LiO}_2$  Glasses," Paper 12-GP-87F, Amer. Ceram. Soc. Glass Division Meeting, Bedford Springs, PA (1987).
24. S.D. Fantone, Design, Engineering and Manufacturing Aspects of Gradient Index Optical Components, Doctoral Thesis, University of Rochester, 1979.
25. D.P. Ryan-Howard, Chromatic Properties of Index of Refraction Gradients in Glass, Doctoral Thesis, University of Rochester, 1983.
26. R.H. Doremus, "Optical Properties of Small Silver Particles," J. Chem. Phys., v.41, p414 (1965).
27. S. Ohmi, et al, "Gradient Index Lenses Made by Double Ion Exchange Process," Appl. Opt., v.27, p496 (1988).
28. M. Yamane, et al, "Preparation of Gradient-Index Glass Rods by the Sol-Gel Process," J. Non-Cryst. Sol., v.85, p244 (1986).
29. K. Shingyouchi, et al, "Radial Gradient Refractive Index Glass Rods Prepared by a Sol-Gel Method," Elec. Lett., V.22, p99 (1986).
30. K. Shingyouchi, et al, "R-GRIN  $\text{TiO}_2\text{-SiO}_2$  Glass Rods Prepared by a Sol-Gel Method," Elec. Lett., V.22, p1108 (1986).

31. L.R. Gardner and D.T. Moore, "Athermalization: A theoretical study of radial GRIN lenses using glassy polymers," paper J2 from 6th Topical Meeting on Gradient-Index Optical Imaging Systems, Palermo, Italy (1985).
32. Y. Ohtsuka and Y. Koike, "Studies on the light-focusing plastic rod. 16: mechanism of gradient-index formation in photocopolymerization of multiple monomer systems," *Appl. Opt.*, v.23, p1774 (1984).
33. L.R. Gardner and D.T. Moore, "Fabrication of polymer radial index gradients utilizing a new cross-linking polymer," paper ThD2 from 7th Topical Meeting on Gradient-Index Optical Imaging Systems, Reno, NV (1987).
34. M. Toyama, et al, "Gradient index objective for the compact disk," paper F1, from 6th Topical Meeting on Gradient-Index Optical Imaging Systems, Palermo, Italy (1985).
35. P.R. Yoder, Jr., "Design of two new lightweight military binoculars," *J. Opt. Soc. Amer.*, v.50, p441 (1960).
36. J.B. Caldwell, "Gradient-index binocular objective design," *Appl. Opt.*, v. 25, p3345 (1986).
37. D.S. Kindred and D.T. Moore, "Design, fabrication, and testing of a gradient-index binocular objective," *Appl. Opt.*, v.27, p492 (1988).