

Radial GRIN glasses in $\text{Li}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ systems

N. SOODBISWAS

Central Glass and Ceramic Research Institute, Calcutta-700 032, India

S. K. SARKAR, A. BASURAY

Department of Applied Physics, University of Calcutta, 92 APC road, Calcutta-700 009, India

A series of GRIN glass rods have been developed in $\text{Li}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ systems. Negative radial refractive index profiles were generated by exchanging Na^+ for Li^+ ions in these glass rods. It has been observed that TiO_2 plays a vital role in increase in the profile depth and maximum change in the refractive index because of its ambivalent nature. Change in the refractive index can be further increased by increasing the concentration of exchanging cation in the base glass. © 1998 Kluwer Academic Publishers

1. Introduction

Radial GRIN lenses having lower refractive index at the rim and higher toward the centre (negative refractive index profile) are used as imaging lenses in copier, facsimile, fibre couplers and compact disc lenses. A long radial GRIN with negative refractive index profile focuses the light beam at a large number of points longitudinally shifted among themselves on the optic axis and thus behaves like a number of micro-lenses arranged in tandem. These GRIN rods translate image through themselves and are being used as endoscopes [1]. However, the application of GRIN lens is limited by the availability of only a few varieties. Although a large number of designs using GRIN elements are available for cameras, microscopes, and binoculars providing better imaging and packaging, practical fabrication is difficult due to the non-availability of GRIN lenses in various refractive index ranges. The exploitation of GRIN optics calls for the generation of pre-specified refractive index profiles in different types of base glasses. The most common method for fabrication of GRIN lenses is the ion exchange technique because of its procedural simplicity. In this method, variation in refractive index within the glass is generated by dipping a piece of glass in a molten salt bath at a temperature close to its glass transition temperature. The glass surface acts as a cation selective interface. The ions so exchanged at the surface diffuse inward and create spatial variation in the glass composition. Localized change in composition is responsible for the change in refractive index within the glass piece. GRIN elements using both crown and flint base glasses are needed to cover the wide range of refractive indices. Both positive and negative GRIN elements may be developed in these base glasses. However, it is interesting to note that a GRIN rod with nearly parabolic profile and having maximum refractive index at the centre can be used either as a converging or diverging lens system by changing its length [2]. In this paper, work on development on negative radial GRIN in titania flint is reported.

2. Choice of base glass

Selection of a base glass for ion exchange is critical to achieve the desired changes in refractive index in the glass [3]. Electrochemical activities between the exchanging ions, bond strength of alkali ions in the base glass and the relative mobility of ionic species within the glass network are the factors that influence ion exchange reaction rate. The choice of the base glass as well as the salt system should be such that substantial diffusion can be achieved in a reasonable time. In general, glasses contain three kinds of oxides: glass formers (e.g., SiO_2 , P_2O_5 , B_2O_3 , GeO_2 etc.), modifiers (e.g., Na_2O , Li_2O , K_2O , Tl_2O , Ag_2O etc.) and intermediates (e.g., Al_2O_3 , TiO_2 , PbO , BaO etc.) In silicate glasses, ion exchange is best achieved by monovalent modifiers, as they are the most mobile ions in the glass. Mobility of the singly charged cations can be further enhanced by replacing part of the glass former SiO_2 by the intermediates like Al_2O_3 , where Al^{3+} replaces Si^{4+} in SiO_4^- tetrahedron. This reduces the number of non-bridging oxygen atoms associated with the monovalent cations, and thus makes the monovalent cations more mobile until the concentration of Al^{3+} ions is equal to or less than the concentration of monovalent cations [4]. The refractive index of the glass can be increased by incorporating PbO or TiO_2 in the glass during melting. Though glasses containing PbO have a much higher refractive index, they possess poor ionic mobility, making them unfit for ion exchange. Incorporation of the Ti^{4+} ion as TiO_2 in silica glass replaces SiO_4^- tetrahedra by TiO_4^- tetrahedra, and therefore has little or no effect upon the mobility of the monovalent cations [5]. In the $\text{TiO}_2\text{-Na}_2\text{O-SiO}_2$ glass system, titania plays an ambivalent role by acting as both network former and modifier [6]. The concentration of TiO_4^- tetrahedra decreases and that of TiO_6^- octahedra increases with increasing alkali content [7]. Moreover, TiO_2 in the glass structure increases the refractive index, decreases the thermal expansion of the glass and facilitates ion exchange as well as the diffusion process due to its ambivalent

TABLE I Composition (mole %) of NG3A2 & NG3B2 glasses and their properties

	NG3A2	NG3B2
SiO ₂	53.4	50.6
Al ₂ O ₃	4.5	4.3
TiO ₂	11.5	11.0
Na ₂ O	20.3	14.6
Li ₂ O	10.3	19.5
r.i. (546.1 nm)	1.6175	1.621
Abbe value	26.68	27.62
T _g °C	456	455
α _{50/300} per °C	124 × 10 ⁻⁷	127 × 10 ⁻⁷

nature [7]. Therefore, the choice of base glass for producing refractive index variation in the glass by the ion exchange technique in the higher refractive index range would be glasses in the R₂O-Al₂O₃-TiO₂-SiO₂ system, where R₂O = Na₂O + Li₂O. Glasses containing lithia only devitrify with ease, and hence do not form stable glass suitable for ion exchange experiments. In order to obtain a lower refractive index at the surface, Li⁺ ions in the glass are exchanged with Na⁺ ions from the molten NaNO₃ salt bath as an increase in molar volume decreases the refractive index.

3. Glass preparation

Two base glasses, NG3A2 and NG3B2, were melted as shown in Table I, using optical grade Na₂CO₃, Li₂CO₃, TiO₂, SiO₂ and Al₂O₃ in platinum crucibles at 1350 °C for 2 h. This cullet (approximately 400 gm) was remelted in platinum crucibles for 24 h at 1400 °C in a platinum wound electric furnace. Glasses were poured at 1200 °C into preheated cast iron moulds and annealed at 500 °C for an hour. The slabs were then cooled slowly to room temperature. The glass slabs were free from bubbles and stresses. Thermal expansion and glass transition temperatures were measured with an Orton dilatometer. Refractive indices at different wavelengths were measured with a Pulfrich refractometer, and then Abbe values were calculated as shown in Table I. Glasses containing still higher Li₂O could not be melted, as they are prone to devitrification.

4. Ion exchange experiments

Glass rods of 6 mm diameter were fabricated from NG3A2 and NG3B2 glasses. These rods were again annealed at 500 °C for 12 h for removal of stresses generated during shaping. The glass rods of length 15 to 20 mm were then dipped into salt baths containing 25.5 gm of NaNO₃ at 370 °C and 400 °C respectively in an electrically heated tubular furnace with a temperature control within 2 °C for different durations as shown in Table II. To maintain consistency in heating and cooling of the salt, the same furnace was used for all the experiments. New salt and crucibles were used for each experiment. The glass rods were then removed from the salt bath and cooled slowly to room temperature. Salts attached to the rods were removed by washing with warm water.

TABLE II Ion exchange parameters of NG3A2 & NG3B2 glasses

Glass No.	Exchange duration	Exchange temp.
NG3A2-S01	50 h	370 °C
NG3A2-S02	100 h	370 °C
NG3A2-S03	150 h	370 °C
NG3B2-S01	50 h	400 °C
NG3B2-S02	100 h	400 °C
NG3B2-S03	150 h	400 °C

5. Refractive index profile measurement

The refractive index profile of these glasses were measured by a method developed earlier [8]. In this method, circular fringes from interference between two longitudinally shifted point sources are generated with the help of a birefringent lens. The basic property of birefringent material having two refractive indices for ordinary and extraordinary rays is employed to produce two longitudinally shifted point sources. The interference pattern is then made to pass through the radial GRIN sample to be tested. The output pattern will diverge or converge depending upon the type of GRIN it encounters. From the deviation of the pattern, refractive index variation can be measured.

6. Results and discussion

Figs 1 and 2 show the refractive index profiles generated in glasses NG3A2 and NG3B2. In the present glass systems, the maximum change in refractive index

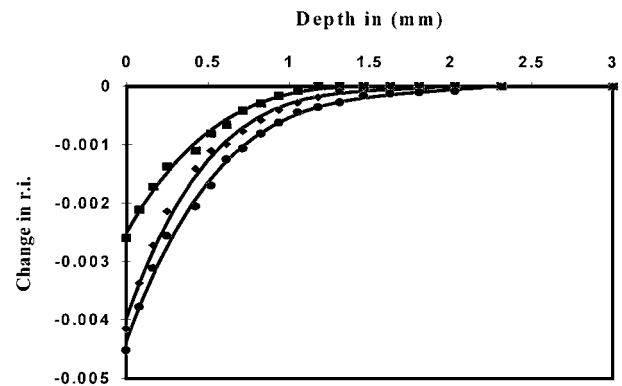


Figure 1 Refractive index profiles in NG3A2 negative GRIN rods ■ NG3A2-S01, ◆ NG3A2-S02 and ● NG3A2-S03.

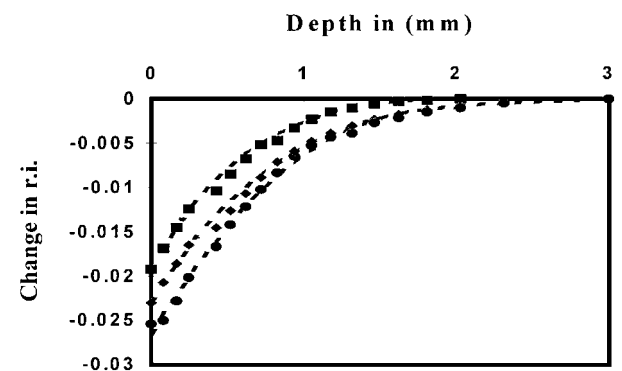


Figure 2 Refractive index profiles in NG3B2 negative GRIN rods ■ NG3B2-S01, ◆ NG3B2-S02 and ● NG3B2-S03.

does not show any sign of saturation as is observed by Kindred *et al.* [9] in $\text{TiO}_2\text{-Li}_2\text{O-Na}_2\text{O-SiO}_2$ glass. Reduction in the maximum change in refractive index with increase in the soaking duration occurs as the ion exchange moves towards completion. However, present studies show that the ion exchange process did not move towards equilibrium even when the glasses were soaked in the salt bath for 150 h. Inclusion of TiO_2 increased profile depth as well as the maximum change in refractive index. Presence of titania in glass plays an important role in producing refractive index variation in glass by the ion exchange process. The refractive index profile for the glass NG3A2-S03 (Fig. 1) shows that 11.5 mole % of titania in the base glass can provide a refractive index variation of 0.0045 with a profile depth of about 2 mm, even at the soaking temperature of 370 °C. The base glass NG3A2 is comparable to the glass described in [8], wherein the base glass does not contain titania. 50 h soaking duration at 370 °C has increased the maximum change in the refractive index from 0.00092 as in [8], to 0.0026 in NG3A2, and the profile depth has also gone up from 0.85 mm to 1.2 mm. This effect was also observed by Kindred [10] while developing a positive GRIN profile in the $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ system. However, ion exchange was carried out at a higher temperature (500 °C) than that in the present study (370 °C). It has also been observed in the present studies that a decomposition of NaNO_3 takes place above 400 °C, and the salt volatilizes out.

With increased lithia content to 19.5 mole percent, the maximum change in refractive index achieved is 0.026 and the profile depth is 3 mm, at the soaking temperature of 400 °C. Both the maximum Δn and profile depth are higher than that reported by Kindred *et al.* in

the $\text{TiO}_2\text{-Li}_2\text{O-Na}_2\text{O-SiO}_2$ glass system. Alumina addition increases the mobility of monovalent cations in the glass, and may be the probable cause of the increase in the refractive index variation as well as the profile depth.

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