Soda-Lime Glass with Gradient of Refraction Index (GRIN)

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In a soda-lime glass provided by Companhia Vidraria Santa Marina, subsidiary of French Saint-Gobain, we induced a gradient of refraction of index (GRIN) by exchange of Na^+ in glass by Li^+ at 550^{o}C for 12, 24, 36 and 48 hours and varying bath temperature at 525^{o}C, 550^{o}C, 575^{o}C and 600^{o}C for fixed time of 48 hours. Δn = 0.0107 $\pm$ 0.0005 and GRIN depth of about 2.4mm were obtained for the ion exchange at 550^{o}C for 48 hours. The GRIN profile was fitted with $erfc(x)$ function and then obtained the diffusion coefficient $D = (1.6 \pm 0.3) \cdot 10^{-6}$ mm^2/s.

I Introduction

The so called optical glasses have been traditionally homogeneous. During last thirty years, glasses having index of refraction varying with spatial coordinates have been introduced. Ion exchange in glasses was discussed by Garfinkel [1] and Doremus [2] in 1968 and 1969, respectively. Problems concerning optics of GRIN glasses have been treated by Sands [3, 4], Moore and Sands [5], and Kapron [6] in the early 70's. Several techniques have been used for manufacturing GRIN glasses such as neutron irradiation, chemical vapor deposition, polymerization techniques, ion exchange, ion stuffing and sol-gel process. CVD technique has been used to produce GRIN fibers for telecommunications [7]. Ion exchange is probably the most widely used technique due to its relatively simple one compared to other processes. Ion stuffing consists in using a special glass that when heated, its phases separate [8]. One of these phases is dissolved in an acid leaving a porous glass, then it is stuffed with ions or molecules in such a way that a gradient composition is produced. Sol gel process can be used in fabricating GRIN rods with large geometry [9]. The gradient in the refractive index can be produced in the radial, axial or spherically symmetrical direction. Such GRIN elements have been used in copiers, facsimiles, endoscopes, etc. Several kinds of base glasses have been investigated. For exchange, Li^+, Na^+ K^+, Tl^+, Ag^+ ions are frequently used [10].

II Experiments and results

Samples of soda-lime glass fabricated by Comp. Vidraria Santa Marina in S. Paulo, was used in the present work. Its composition is: $72SiO_2$ - $9CaO$ - $13Na_2O$ -$4MgO$ - Al_2O_3 with small amounts of Fe_2O_3, TiO_2 and K_2O (these three compounds totaling about 1% weight are also found). The refractive index of this glass was found to be n_o = 1.5213 $\pm$ 0.0005. The ion exchange method was used for inducing the gradient of refractive index. Initially, we used a bath of molten of LiCl for the exchange $Li^+ \leftrightarrow Na^+$ of the glass. The melting point of LiCl is 600^{o}C, and since for soda-lime glass $T_g \sim 610^o$C, immersing the glass into LiCl melt the glass devitrified strongly. We then followed Kindred et al. experiments [10], in which to lower the bath temperature, $CaCl_2$ was mixed. They used an eutetic mixture of $60CaCl_2$ - 40LiCl with melting temperature of 496^{o}C. In the present work the samples were kept immersed in such a bath at 550^{o}C and varying time of ion exchange, Fig. 1, and varying bath temperature for

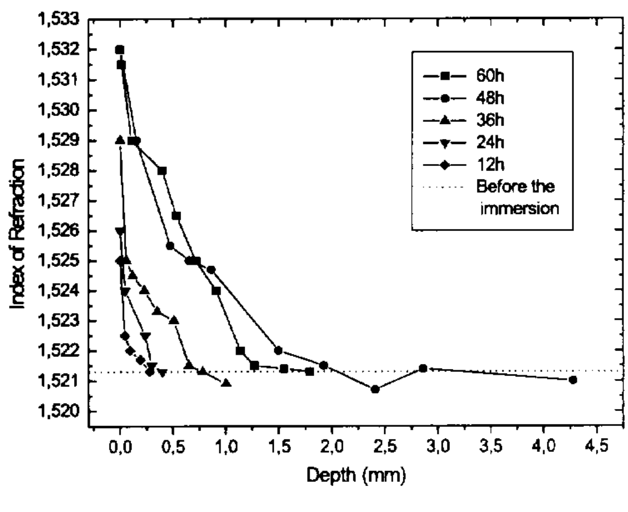

Figure 1. GRIN profiles for different times of ion exchange (550^{o}C).

fixed 48 hours exchange time, Fig. 2. After ion exchange process the samples were cooled at room temperature. The glass presented crystallization characterized by milky colour. A surface layer was removed to eliminate devitrified portion. X-ray diffractogram indicates that the remaining part of the glass is amorphous. The measurement of variation of the refractive index n with depth was carried out removing successive layers and measuring n each time.

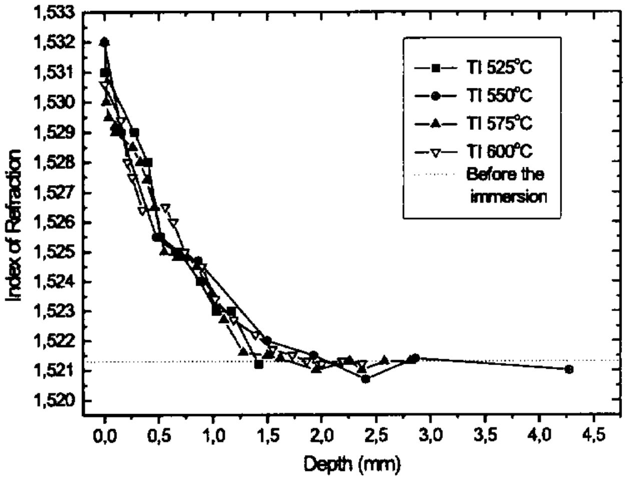

Figure 2. GRIN profiles for different temperatures for fixed time of exchange (48 h).

III Ionic diffusion and GRIN

Fick's laws describe the ions diffusion in a solid. Denoting by $C(x,t)$, the concentration of diffusing species at depth x and at instant t, by $D(T)$ the diffusion constant at temperature T, the solution of Fick's laws for $D(T)$ constant at T is given by:

$$C(x,t) = C_0 \cdot erfc\left(\frac{x}{\sqrt{4Dt}}\right) \tag{1}$$

where

$$\begin{aligned} C(x=0, t \geq 0) &= C_0 \\ C(x>0, t=0) &= 0 \end{aligned} \tag{2}$$

The refractive index of a GRIN glass is then dependent on $C(x,t)$ [11]:

$$n(x,t) = n_0 + \Delta n \cdot erfc\left(\frac{x}{\sqrt{4Dt}}\right) \tag{3}$$

Fig. 3 presents the GRIN profile for 48 hours and 550^oC with depth of about 1.95 ± 0.05 mm.

The full curve in Fig. 3 is the best fit of experimental data, using the equation 3. The refractive index at the surface $n_0 = 1.5210 \pm 0.0005$, the maximum variation of n, Δn $= 0.0107 \pm 0.0005$ and the diffusion coefficient D $= (1.6 \pm 0.3)\cdot 10^{-6}$mm^2/s were obtained from this best fit.

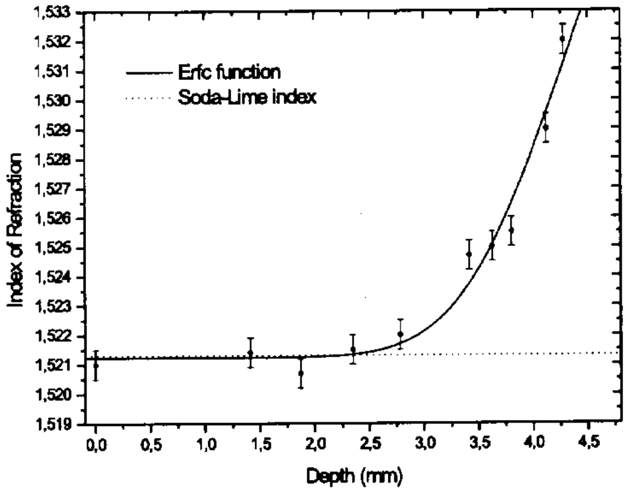

Figure 3. Axial GRIN profile produced by Li^+ for Na^+ exchange in a soda-lime glass for 48 hours and 550C^o.

IV Ray tracing

In Fig. 4, a laser beam is incident on a slab of GRIN glass with thickness L. α being the angle of incidence of laser beam and θ_o the angle of refraction at the entrance surface, after reaching GRIN region, at any point x, according to Snell's law:

$$n_{air} \cdot \sin\alpha = n_0 \cdot \sin\theta_0 = n(x) \cdot \sin\theta(x) \tag{4}$$

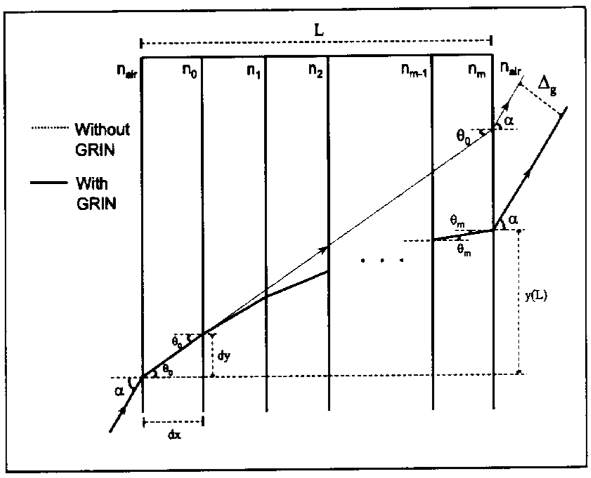

Figure 4. Laser beam incident on a slab of GRIN glass.

where x is measured from beginning of GRIN and perpendicular to slab surface. The ray emerges at an angle α with respect to the normal to glass surface. Since in an homogeneous glass with refractive index n_0, the ray entering under angle α emerges also forming an angle α, the effect of GRIN is to produce a displacement Δ_g of emergent ray compared to emergent ray from a glass without GRIN. A numerical calculation using the equation 4 produced for GRIN glass obtained here, a value of about $\Delta_g \sim 0.00202$mm for $\alpha \sim 57^o$. Experimentally, this is a value too small to be measured due to the laser beam diameter. The table 1 lists values of Δ_g for α between 30 and 80^o. The Fig. 5 shows the variation of Δ_g as function of α.

Table 1. Δ_g as function of the incidence angle α.

α (degrees)	Δ_g (mm)
30	0.00132
36	0.00156
42	0.00177
45	0.00185
51	0.00198
54	0.00201
57	0.00202
60	0.00200
63	0.00195
69	0.00174
75	0.00139
81	0.00090

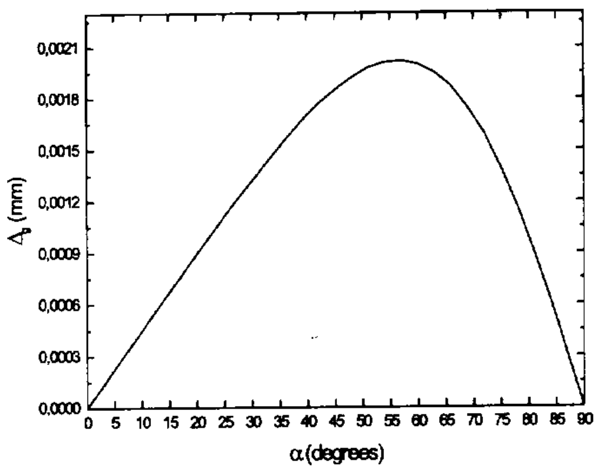

Figure 5. Variation of Δ_g as function of α.

V Discussion and Conclusion

According to Kindred [11], in many cases the refraction index is linearly dependent on the concentration. This is the present case. With the exchange $Li^+ \leftrightarrow Na^+$, Haun et al. [12] did not fit the the GRIN profile with erfc(x) as we did. Fig. 1 has shown that both the depth of exchange and the variation Δn of the index of refraction increase with the time of exchange, however, the result shown in Fig. 2 indicated that for fixed time of 48 hours, the depth of exchange and Δn did not change with temperature in the range 525^oC and 600^oC. This last result is due to the increase in the thickness of crystallized layer. The maximum variation Δn and largest depth of exchange were obtained for time between 48 and 60 hours at 550^oC, as well as for 48 hours at temperature between 550^oC and 575^oC. For 48 hours at 550^oC, $\Delta n = 0.0107 \pm 0.0005$ and a depth of 1.95 ± 0.05 mm were obtained. At this temperature a coefficient of diffusion of Li^+ with value D = $(1.6 \pm 0.3)\cdot 10^{-6}$mm^2/s was obtained. Meyer-Arendt [13] suggested the use of GRIN glass to eliminate spherical aberration. Grinding and polishing the GRIN glass region a preliminary result showed a lens without spherical aberration.

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