Strengthened glass by ion exchange, mechanical and optical properties: perspectives and limits of glass as a substrate for flexible photonics

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ABSTRACT

Flexible photonics is an emerging technology in photonics applications. The availability of ultra thin glasses with thicknesses ranging from tens to hundreds of microns is an appealing opportunity to be considered for flexible photonics applications substrates. The increase in mechanical characteristics, specifically strength, for such glasses is achieved by specific chemical compositions and ion exchange processes. The main physical effects to be considered are the introduction of residual stress profiles and refractive index modifications. Both aspects may interfere with flexible photonics applications of these glass substrates. There will be discussed the underpinning physics of stress build up and relaxation and how these effects may affect refractive index. The discussion will be mainly focused to the most promising glass chemical compositions already widely used in consumer electronics applications that is sodium aluminosilicates.

Keywords: Glass, flexible photonics, ion exchange, residual stress, refractive index.

1. INTRODUCTION

Glass in photonics applications is a subject recording a growing interest in the literature. Among photonic materials glasses play a significant role. Considering photonic applications glasses are considered in:

- Solid state laser with the so called “laser glasses”, which are multicomponent oxide glasses suitably doped with rare earth ions, mostly lanthanides, in order to amplify light by stimulated emission of radiation.
- Optical fibers, that is dielectric waveguides made of high purity glasses that are critical components in photonic applications such as lasers, amplifiers and sensing.
- Functional photonic circuits that, suitably integrated in “chip-scale platforms”, are the elements of integrated photonics. These devices take advantage of optical and structural properties of glass which are the building blocks of the systems.

Such materials for photonics applications are considered in either bulk, thin film, or fiber form. In recent times it has been proposed the use of high strength glasses for flexible integrated photonic devices that can be bend, twisted or stretched without compromising structural integrity and optical performances. Materials and devices proposed are bendable chalcogenide glass waveguide circuits and flexible nano-membrane glass waveguide photodetectors. In the present study a class of high strength glasses is presented with the potential to be used as substrates for photonic devices. These are ultra thin sodium alumino silicate glasses developed for consumer electronics and already introduced in the market since several years. The capability to bend glass with very low bending radii limits the maximum thickness that can be practically considered. The bending radius limit that can be achieved is dictated by the mechanical properties of the glass. It is well known that strength is not an intrinsic material property of glass, it is mainly related to the presence in the surface of flaws that can be nucleated at the forming process and than developed during the article formation. Glass under extreme bending develops high tensile stress that may lead to immediate breakage or delayed breakage due to subcritical crack growth mechanisms. This last phenomenon is known as static fatigue and it is driven by the presence of tensile stress and water vapor that, penetrating to the tip of the surface flaws, enhance silicon-oxygen bond breakage resulting in a flaws depth increase. These mechanisms are described in terms of fracture mechanics through the stress intensity factor concept which depends on stress level, flaw depth and flaw geometry. Glass failure is instantaneous as strength is not an intrinsic material property of glass, it is mainly related to the presence in the surface of flaws that can be nucleated at the forming process and than developed during the article formation. Glass under extreme bending develops high tensile stress that may lead to immediate breakage or delayed breakage due to subcritical crack growth mechanisms. This last phenomenon is known as static fatigue and it is driven by the presence of tensile stress and water vapor that, penetrating to the tip of the surface flaws, enhance silicon-oxygen bond breakage resulting in a flaws depth increase. These mechanisms are described in terms of fracture mechanics through the stress intensity factor concept which depends on stress level, flaw depth and flaw geometry. 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glasses. For alkali containing glass a threshold limit exist for the activation of subcritical crack growth (SCG) phenomena. In order to keep glass article under long term bending stress, there are two possibilities: using alkali free glasses with a nearly pristine glass surface with flaws not exceeding depth of few microns. In this case it is imperative to have a complete sealing of the tensile stressed surface such that no water vapor can reach flaws tip activating subcritical crack growth. Another possibility is using alkali silicate glasses to be strengthened by the introduction of residual stress by ion exchange. In this last approach surface flaws are sealed within the near surface compressive layer introduced by ion exchange. In this study they are presented the limitations in term of thickness for the two glass types candidates for extreme bendable applications. The analysis is performed by considering stability conditions of surface flaws under both applied high tensile stress and residual surface compression stress intentionally introduced. It worth notice that highly bendable glass has already been considered in applications of foldable organic light emitting diode (OLED) display technology. In display technology applications, glasses present advantages over the initially considered polymeric materials in terms of: elasticity, higher hardness, touch functionality, optical wavelengths transmission and hermeticity.

2. BENDABLE GLASS – MECHANICAL PROPERTIES

Extreme bending capability of glass plate is the requisite to have flexible substrates in electronic or photonic applications. The extreme situation is to have a plate that can be bend at an angle of 180° as shown in figure 1. The functionality requirement is that glass do not fail either immediately or in a time delayed scenario. This is analyzed in terms of mechanical stability for both immediate breakage and delayed breakage due to fatigue effects generated by subcritical crack growth (SCG). Two conditions can be considered: glass not strengthened by residual stress and glass strengthened by the introduction of a residual stress within the glass plate cross section.

2.1 Bendable glass – Strength limit

An inorganic glass plate with a thickness \( d \) in a full bending status, as depicted in Figure 1, with a plate separation \( H \) and a bending radius \( \rho \) at the neutral axis, is exposed to failure due to breakage. The breakage condition can be defined by the glass strength.

![Figure 1. Glass plate of thickness d bended to a plate separation H and reaching a bending radius of \( \rho \) at the neutral axis of the plate.](image)

The extreme bending geometry introduces a bending stress across the glass plate cross section. A relationship between thickness \( d \), plate separation \( H \) and bending radius \( \rho \) can be set up as follows:

\[
H - d = 2.396 \cdot \rho .
\]

(1)

Defining the elastic constants of glass: \( E \) (Young Modulus) and \( v \) (Poisson ratio), the maximum tensile stress \( \sigma_M \) introduced in the bent area of the glass plate is:

\[
\sigma_M = \frac{E}{1-v^2} \cdot \frac{d}{2} \cdot \frac{1}{\rho} .
\]

(2)

Considering a glass plate of thickness \( d = 100 \mu m \), forcing the plate to a separation \( H \) at 15 mm (15000 \( \mu m \)) and considering a glass with \( E = 73.3 \) GPa and a Poisson ratio \( v = 0.216 \) the maximum tensile stress introduced in the bending is \( \sigma_M = 589 \) MPa. This tensile stress is such to lead to an immediate breakage of the glass which has a strength...
(measured in air at room temperature) around 200 MPa. Reducing the thickness of the plate to 50 µm the stress introduced, which is linearly depending from thickness according to equation (2), is still too high when compared to the glass strength. The strength limit above identified can be overcome by further reducing thickness or by considering strengthening processes. Due to the shallow glass thickness, ion exchange is the most viable strengthening process. To reduce the stress below the strength limit the thickness shall be reduced to \( d = 30 \mu m \) with a bending radius of 6.2 mm. The maximum bending stress in this case, according to equation (2), is 184 MPa. The stability of surface flaws can be studied by considering the stress intensity factor \( K_I \) generated by the stress induced in the bending condition and comparing it with the critical value \( K_{IC} \) and the threshold value for subcritical crack growth (SCG) \( K_{Ith} \). The applied stress by bending along the glass plate can be expressed:

\[
\sigma_{appl}(x) = \sigma_m \cdot \left(1 - \frac{x}{d}\right). \tag{3}
\]

Using fracture mechanics, the stress intensity factor for a surface flaw “a” in the stress field (3) can be calculated as:

\[
K_I(a) = \frac{2Y\sqrt{a}}{\pi} \int_0^a \frac{\sigma_{appl}(x)}{\sqrt{a^2 - x^2}} \, dx. \tag{4}
\]

In Figure 2 the plot of \( K_I(a) \) versus the surface flaw depth “a” is reported.

![Figure 2 – Stability diagram KI(a), for a 30 µm glass plate bend with a separation plate of 15 mm](image)

From figure 2 it comes that system is stable not considering fatigue effect that may trigger SGG mechanisms. The main conclusion achieved is that, without strengthening, the thickness limit to achieve the mechanical situation of Figure 1 is a maximum thickness of 30 µm, a surface as pristine as possible and a totally sealed arrangement.
2.2 Bendable glass – Strengthening by Ion Exchange.

The possibility to introduce a residual stress in a glass article strongly influences its capability to withstand extreme bending and, up to a certain limit, may overcome the limitations described in section 2.1 for not strengthened glass. The most suitable technological process for ultra thin glass is ion exchange\textsuperscript{4,5,9}. In order to implement this process the glass chemical composition shall have a certain amount of alkali ions to be exchanged. Typical composition are based on alkali aluminosilicate glass with lithium or sodium as typical alkali elements. Herewith we will consider sodium aluminosilicate glass to be ion exchanged in potassium nitrate molten bath where sodium ions in the glass are replaced by potassium ions coming from the bath. The underpinning physics of this process has been reviewed in the literature\textsuperscript{4,6,11} while the matter related to stress buildup and relaxation has been extensively discussed\textsuperscript{12} identifying the relevant relaxation mechanisms that justify some anomalous behavior recorded in the literature. The discussion below is focused in the glass type of reference [9] which is a sodium aluminum silicate. This glass is designed with a chemical composition and a forming process specifically suitable for ion exchange of sodium ions in the glass for potassium ions coming from the molten salt source where the glass is immersed for a certain time and at a defined temperature. This process modifies the chemical composition of the glass in a near surface layer where we record an increase of potassium concentration with a corresponding reduction of the sodium one. The resulting concentration profiles can be either measured by Electron Micro Probe Analysis (EMPA) techniques\textsuperscript{15} or predicted by computational methods based on diffusion theories in solids\textsuperscript{5,11,12,13,14}. In the majority of the diffusion studies related to ion exchange in glass, ion concentration is expressed through the complementary error function with argument $x/[2 \cdot \sqrt{D \cdot t}]$, where $x$ is the spatial coordinate, $t$ is time and $D$ is the interdiffusion coefficient. This solution is based on the approximated assumption of semi-infinite medium. This last assumption is justified as far as the diffusion length\textsuperscript{12}, $L_D = \sqrt{D \cdot t}$, is far smaller than plate thickness ($L_D << d$). Because of the shallow thickness of ultrathin glass plates, $d$ results comparable with $L_D$ resulting in a not negligible interference of the diffusion fluxes coming from the opposite surfaces. For this reason it is preferred to calculate concentration in the slab geometry\textsuperscript{12,13} instead of taking the usual approximation of semi-infinite medium. The invading ions entering the glass structure by the ion exchange process generate by the enforcement of compatibility conditions an equibiaxial residual stress profile that can be calculated according to the mathematical model introduced by Macrelli, Varshneya and Mauro\textsuperscript{9,10}:

$$
\sigma_{EB}(x,t) = -\frac{E \cdot BC}{1-\nu} \left[ c(x,t)V(x,t)-c_m \right] - \int_0^t \frac{b}{\tau} \left( \frac{t-\theta}{\tau} \right)^{b-1} \exp \left[ -\left( \frac{t-\theta}{\tau} \right)^b \right] \left( c(x,t)V(x,t)-c_m \right) d\theta .
$$

(5)

Where $V(x,t)$ is the Varshneya factor\textsuperscript{9,10} $V(x,t) = V_0 \cdot \Psi c(x,t)$. This factor has been introduced\textsuperscript{10} to account for relaxation mechanisms and $c_m$ is the averaged weighted concentration:

$$
c_m = \frac{1}{d} \int_0^d c(x,t) \cdot V(x,t) dx .
$$

(6)

Residual stress calculated\textsuperscript{5} according to equation (5) with the parameters of Table 1 is presented in figure 3.
From the residual stress profile of figure 3 two main characteristics (Surface compression – \( S_C \) and Compression layer depth \( C_d \)) are evaluated: \( S_C = -849 \) MPa and \( C_d = 19.1 \) µm. These values are quite comparable with the ones measured on a similar glass type: \( S_{C\text{meas}} = -850 \) MPa, \( C_{d\text{meas}} = 20 \) µm. It is worth notice that the ion exchange kinetics, expressed by the interdiffusion coefficient, is particularly enhanced for ultra thin glass. Thin can be addressed to the higher fictive temperature of glasses with such a thin thickness, in this case fictive temperature increase is due to the need of a faster and highly controlled cooling during the flat glass forming process typical of down draw and overflow fusion processes. The improved ion exchange kinetics is a key point to achieve a deeper compression layer that is normally reduced in a thinner glass because of the enforcement of compatibility criteria. This last remark is particularly meaningful when considering glass with a reduced thickness by mechanical or chemical etching processes, in these last cases fictive temperature is not changed and ion exchange kinetics is expected to be the same of the parent thicker glass. The compression layer depth reduction due to a thickness reduction of one order of magnitude (from 1mm to 100 µm) with same interdiffusion kinetics is expected to be around 30%.
Table 1. Main physical parameters considered in the simulation.

<table>
<thead>
<tr>
<th>Physical Characteristics</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>E - Young modulus</td>
<td>GPa</td>
<td>73.3</td>
</tr>
<tr>
<td>v - Poisson ratio</td>
<td>adimensional</td>
<td>0.216</td>
</tr>
<tr>
<td>D – interdiffusion coefficient at 390°C</td>
<td>µm²/s</td>
<td>0.02</td>
</tr>
<tr>
<td>τ - Stress Relaxation time at 390°C</td>
<td>s</td>
<td>7.5 × 10⁸</td>
</tr>
<tr>
<td>b – exponent of the stretched non-Maxwellian relaxation function</td>
<td>adimensional</td>
<td>3/7</td>
</tr>
<tr>
<td>B·C – Strain generated by ions invasion</td>
<td>adimensional</td>
<td>0.0162</td>
</tr>
<tr>
<td>Vo – Constant of Varshneya factor</td>
<td>adimensional</td>
<td>0.89</td>
</tr>
<tr>
<td>Ψ - Coefficient of the Varshneya factor</td>
<td>adimensional</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The next analysis is to consider this chemically strengthened glass in an extreme bending condition as reported in figure 1. Following the same approach of the not strengthened plate and considering a surface flaw of depth “a”, we can study its stability within the residual stress represented in figure 3, \( \sigma_{EB}(x) \), and with an externally applied stress (3) coming from the extreme bending condition. The effective stress field is now the superposition of the external bending stress internal residual stress:

\[
\sigma_{net}(x) = \sigma_{appl}(x) + \sigma_{EB}(x). \tag{7}
\]

The resulting stress intensity factor \( K_I \) is calculated with the new superposition function \( \sigma_{net}(x) \):

\[
K_I(a) = \frac{2Y\sqrt{a}}{\pi} \int_0^a \frac{\sigma_{net}(x)}{\sqrt{a^2-x^2}} \, dx. \tag{8}
\]

The stress function resulting from superposition (7) is plotted in figure 4. Both glass surfaces are under compression even while bent to a 6.2mm bend radius. It is worth notice that the glass surface in the outer side is still in compression (about -200 MPa) and this compression status extends towards the inner part of the glass for about 7-8 microns and a depth of compression layer of about 30 microns on the inner surface. Any surface flaws within the above specified compressive layers is expected to resist to immediate failure and fatigue effects.
Figure 4. Superposition of residual stress generated by ion exchange $\sigma_{EB}(x)$ and external stress due to deep bending $\sigma_{appl}(x)$.

The stability diagram generated from equation (8) is presented in figure 5. Immediate breakage is for surface flaws around 15$\mu$m depth while SGG activates for surface flaws deeper than 10$\mu$m.

Figure 5. Stability diagram of the stress intensity factor $K_I$ as a function of flaw depth $a$ ($\mu$m) for a glass of thickness $d = 100 \mu$m in a stress field generated by a deep bending $\sigma_{appl}(x)$ with a plate separation of $H = 15$mm and bending radius $\rho = 6.25$ mm and a residual stress $\sigma_{EB}(x)$ generated by ion exchange at 390°C for 2 hours immersion time.
The introduction of residual stress by ion exchange results in a stable situation for surface flaws below 10 micron depth even in case of external exposure to water vapor. The high level of compression so introduced enlarge the limit of glass thickness to be used in deep bending to at least 100 microns, also without the need of a water vapour seal.

3. OPTICAL PROPERTIES

The use of ultrathin bendable glass as support for photonics devices deserves an additional attention related to refractive index effects. When glass is under stress refractive index effects may be expected due to birefringency. There is a significant difference of refractive index effects in non-strengthened glasses and refractive index effects in strengthened glasses by ion exchange.

3.1 Refractive index effects in non-strengthened glasses

The relationship between stress and refractive index can be summarized in the well known Maxwell-Werthaim equations:

\[
\begin{align*}
    n_{xx} &= n_0 + \Gamma_1 \sigma_{xx} + \Gamma_2 \sigma_{yy} + \Gamma_2 \sigma_{zz} = n_0 + \Gamma_1 \sigma_{xx} + \Gamma_2 (\sigma_{yy} + \sigma_{zz}) \\
    n_{yy} &= n_0 + \Gamma_2 \sigma_{xx} + \Gamma_1 \sigma_{yy} + \Gamma_2 \sigma_{zz} = n_0 + \Gamma_1 \sigma_{yy} + \Gamma_2 (\sigma_{xx} + \sigma_{zz}) \\
    n_{zz} &= n_0 + \Gamma_2 \sigma_{xx} + \Gamma_2 \sigma_{yy} + \Gamma_1 \sigma_{zz} = n_0 + \Gamma_1 \sigma_{zz} + \Gamma_2 (\sigma_{xx} + \sigma_{yy})
\end{align*}
\]

Where \( \Gamma_1 \) and \( \Gamma_2 \) are the stress-optical coefficients that can be expressed in terms of the Pockels coefficients. Stress generated by bending and residual stress generated by strengthening are both equibiaxial and equations (9) can be simplified accordingly:

\[
\begin{align*}
    n_{xx} - n_o &= 2 \Gamma_2 \sigma_{EB} \\
    n_{yy} - n_o &= \left( \Gamma_1 + \Gamma_2 \right) \sigma_{EB} \\
    n_{zz} - n_o &= \left( \Gamma_1 + \Gamma_2 \right) \sigma_{EB}
\end{align*}
\]

If we have an electromagnetic wave travelling in the z direction (see figure 6), then only \( n_{xx} \) (TM polarization) and \( n_{yy} \) (TE polarization) are relevant.

![Figure 6. Equibiaxial boundary condition representation in the principal axis coordinates.](image)

If we have an electromagnetic wave travelling in the z direction (see figure 6), then only \( n_{xx} \) (TM polarization) and \( n_{yy} \) (TE polarization) are relevant.

The interesting application of equation (10) is in the possibility of determining \( \sigma_{EB} \) through measuring the difference between \( n_{xx} \) and \( n_{yy} \):

\[
\sigma_{EB} = \frac{n_{xx} - n_{yy}}{2} = \frac{n_{xx} - n_{yy}}{\Gamma_2 - \Gamma_1}, \quad (11)
\]
The difference $\Gamma = \Gamma_2 - \Gamma_1$ is the stress optical coefficient (also named Brewster constant). An example of refractive index profile with a superposition of bending and residual stress has been evaluated for the stress distribution of figure 4 and is reported in figure 7.

![Refractive index profiles](attachment:refractive_index_profiles.png)

**Figure 7.** Refractive index profiles for an ultra-thin glass of thickness 100 $\mu$m with a residual stress generated by ion exchange and extreme bending conditions. Curves are shown for $n(x)$ original glass refractive index, $n_p(x)$ refractive index due to polarizability and molar volume changes due to ion exchange and $n_{TM}(x)$, $n_{TE}(x)$ components of refractive index for Transverse Magnetic - TM and Transverse Electric - TE components.

From Figure 7 it results that chemically strengthened glass substrates in extreme bending are optically active materials exhibiting important near surface refractive index gradients.

4. CONCLUSION

It has been carried out a mechanical analysis of a glass plate in extreme bending conditions. Stability characteristics have been studied for either alkali-free not strengthened glasses and sodium aluminosilicate glasses strengthened by ion exchange. Limitations have been identified for the not strengthened glass in terms of thickness (30 $\mu$m for not strengthened glasses) for applications with a bending radius of 6.2 mm corresponding to a total folding at 180° of the plate. Further limitations for alkali free glasses have been identified in the need to have nearly pristine surfaces and in the need of sealing the glass surfaces from water vapour to prevent subcritical crack growth leading to glass breakage by fatigue effects. A similar analysis has been carried out for the sodium aluminosilicate glass strengthened by the introduction of a residual stress via ion exchange. The mechanical analysis has identified specific limitations that, in some extent, enlarge and overcome the limits in thickness and the need of sealing to water vapour found for the alkali free glasses. For photonics applications as substrates for devices handling electromagnetic radiation, effects to optical properties may be relevant. Effects to refractive index modifications have been studied resulting that chemically strengthened glass substrates, in extreme bending, are optically active materials exhibiting important near surface refractive index gradients to be considered in the optical design.
REFERENCES

[16] Frischat, G.H.,[Ionic diffusion in oxide glasses], Trans Tech Publications, Aedermannsdorf (CH), 1975