Strengthening of chalco-halide glasses by ion exchange

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Abstract

In this study was investigated for the first time the efficiency of ion-exchange treatments for strengthening of the chalcogenide glasses. A new generation of chalco-halide glasses transparent from the visible up to the mid-infrared has been ion exchanged by heat treatment below Tg in an ion nitrate melt bath. The exchange depth and the effective diffusion coefficient of Rb^+ and Cs^+ in the $56GeSe_2$-$24Ga_2Se_3$-20KI glass have been measured with a SEM coupled with Energy Dispersive Spectroscopy. The evolution of the mechanical properties was determined using bi-axial flexural strength experiments according to the immersion time in the $50\%KNO_3$-$50\%CsNO_3$ or in the $50\%RbNO_3$-$50\%CsNO_3$ molten salt. An increase of the flexural strength from 17 MPa to 33 MPa is observed after ion exchange. The evolution of infrared transmission can be controlled according to the heat treatment time and temperature. The results described in this paper open a new way to reinforce the weak mechanical properties of chalcogenide glasses.

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Keywords : Ion exchange, Chalco-halide glasses, Mechanical properties

1. INTRODUCTION

Molding of chalcogenide glass is a low cost alternative solution to expensive single crystalline germanium in order to produce lenses for thermal imaging devices. The broad band transmission of selenium based chalcogenide glasses, overspreading the second and third atmospheric window, was recently extended in the visible region by introducing ionic elements such as alkali halide in the Ge-Ga-Se system [1-2]. However, mechanical properties such as resistance to thermal shocks and to crack propagation are known to be a weak point of chalcogenide glasses. We have explored different ways in order to obtain chalcogenide glasses with improved surface hardness and strength:

1- Generate submicron crystals by nucleation and growth phenomena with specific heat treatment. In this way, the generation of Ga_2Se_3 crystals of 100nm length in chalcogenide glass-ceramics based on the $GeSe_2$-Ga_2Se_3-CsCl system has demonstrated significant improvement of toughness, but no consequences on the glass hardness [1].

2- Thermal quenching of the glass surface. This technique is usually used in silicate glass manufactures [3-4]. The weak resistance of chalcogenide glass to thermal shocks leads to a difficult control of air flow without damaging the glass bulk.

3- Lay down a protective coating having a different thermal expansion coefficient [5-6]. This approach has not been investigated.

4- Strengthen the glass surface by ion exchange which is usually used in soda-alumina-silicate glasses [7-13]. This method consists in exchanging ions present in the bulk glass by ions being present in a solution.

The migration of big cations on the glass surface instead of smaller cations provokes a surface compression while the inner glass presents a compensatory stress state. Hence, the glass has improved mechanical parameters. However, the molding process generally performed above the glass transition temperature (T_g) to make lenses should be realized before the ion exchange to avoid the relaxation of mechanical stress.

Many papers report on the ion exchange method [12-13], especially for the planar waveguide preparation in silicate glasses [14-16] but very few in chalcogenide glasses [17]. It has been supposed that chalco-halide glasses belonging to the $GeSe_2$-Ga_2Se_3-MX system (MX=alkali halide) are made of covalently bonded building units such as tetrahedral $GeSe_4$ and triangular $GaSe_3$ sharing Se corners. When introduced into the network, the halide atoms play the role of non-bridging atoms and decrease the network connectivity. The ionic bond between the modifier cations and the aperiodic network is ensured by terminal Se- atoms. Thus, the structure of chalco-halide glasses with the possibility of free movement cations under thermal agitation would allow the glass strengthening by ion exchange.

2. EXPERIMENTAL DETAILS

Glasses in the $GeSe_2$-Ga_2Se_3-KI system were synthesized by melting the constituent elements (Ge, Ga, Se of 99.999% and KI of 99.9% purity) under vacuum in a sealed silica tube of 20 mm diameter. The ampoule was heated up in a rocking furnace to 850°C over 12 hours and then lowered to 730 °C for 2 hours to avoid thermal convection flows during quenching. The sample was annealed 10°C below Tg for 8 hours to minimize inner stress induced by water quenching and finally cooled to room temperature. Glass rods were cut in 2 mm thick slices and polished with a precision of $\lambda/4$ for experimentation.

Transmission measurements were realized with a double beam CARY spectrometer in the visible and near infrared region. A Bomem Fourier transform infrared spectrometer was used in the mid and far infrared region.

Scanning Electronic Microscope (SEM) coupled with Energy Dispersive spectrometer was used to analyze the evolution of glass composition from the surface to the center of the bulk after ion exchange and to observe the glass surface.

Differential Scanning Calorimetry (DSC 2010 TA, heating rate of 10 °C/min up to 500 °C) was used to measure the glass transition temperature (T_g) and the crystallization temperature (Tx) of the glass.

Hardness and tenacity were determined using a Vickers micro indenter MATZUZAWA, with a charge of 100g for 5s. Young's modulus is obtained by measuring the ultrasound propagation speed in the glass. Glass density has been measured using the classical Archimedes technique.

To avoid thermal shocks during glass immersion in the molten salt, the glass and bath are simultaneously heated in a closed pyrex tube under an argon flow in order to prevent glass surface oxidation. At the end of the experiment, the glass sample is removed from the bath and slowly cooled down to room temperature without annealing, to avoid stress relaxation. The glass surface is then washed with distilled water.

The morphology of the glass surface was observed by atomic force microscopy (A.F.M.) (Dimension 3100, Nanoscope V, Digital Instruments, Santa Barbara CA, USA), using standard gold coated V shaped silicon nitride cantilevers and operated in contact mode.

Different techniques can be used to characterize the glass flexural strength after the ion exchange. The bi-axial flexion was chosen instead of the 3 points flexion experiments. In this method, an effort was exerted by a ball on a slice of glass sample. Mechanical tests were performed on KI glass slices of 20 mm diameter and 2mm thickness which were immersed in molten bath at different temperatures for different times. The flexural strength was determined on exchanged glass slices with the bi-axial method from concentric ring-on-ring (16 mm and 18 mm diameter) using a Lloyd LR50K equipped with a 100 N sensor. An average of 10 measures was calculated

3. RESULTS

The boundary of the $GeSe_2$-Ga_2Se_3-KI system has been investigated using IR spectrometer and X-Ray diffraction on synthesized glasses (figure 1). The $56GeSe_2$-$24Ga_2Se_3$-20KI base glass was chosen because of its high resistance to crystallization and its high alkali halide content. This glass composition is situated in the center of the glass forming region. DSC experiments show that the base glass has a glass transition temperature of 336 °C and does not present a crystallization peak below 500 °C.

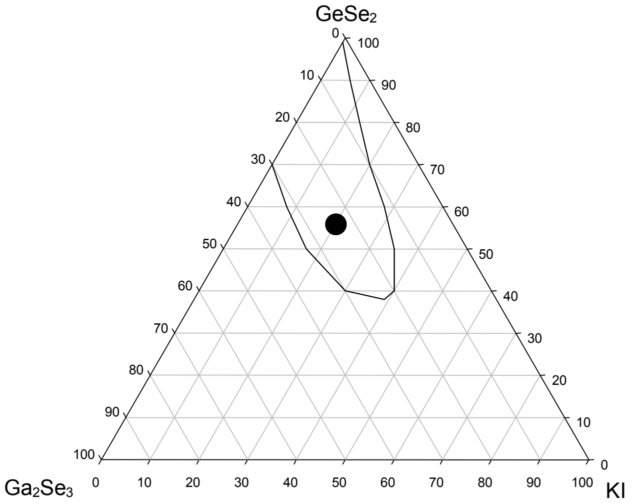

Figure 1. Glass-forming region of the $GeSe_2$-Ga_2Se_3-KI system with the 56$GeSe_2$-24Ga_2Se_3-20KI composition ●).

Experiments to obtain the main thermo-mechanical properties of the 56$GeSe_2$-24Ga_2Se_3-20KI base glass were performed. Results are presented in the Table 1. This glass belongs to the very new generation of glasses transparent from the visible range to the far-IR (16 µm), having a band-gap of 629 nm (E_g=1.99 eV).

Table 1. Thermo-mechanical properties of the 56$GeSe_2$-24Ga_2Se_3-20KI base glass

T_g (°C)	T_x (°C)	Hardness (kg.mm^2)	Density (g/cm^3)	TEC* (MPa.mm½)	Young modulus E (GPa)
336 ± 1	----	160.7 ± 1.3	4.22 ± 0.03	19.0 ± 0.2	16.5 ± 0.2

*Thermal expansion coefficient

Contrary to the alkali-halide molten salts, some nitrate molten salts present a low melting point; they easily dissolve in water, and show no mechanical interaction with chalcogenide glasses. A large difference between the glass T_g and the molten salt melting point allows for a test of ion exchange on a wide temperature range. Experiments were performed by introducing the glass slice in 50$CsNO_3$/50KNO_3 or 50$RbNO_3$/50KNO_3 molten salt. The $CsNO_3$/KNO_3 ratio can vary from 50/50 to 20/80 while maintaining a liquidus temperature lower than 240 °C. A 50/50 ratio was chosen because of its low melting point temperature of 220 °C. The melt of 50$RbNO_3$/50KNO_3 presents a melting point around 295 °C which prevent from using a broad band of temperature. Indeed, the glass could be put out of shape under its own weight when it is warmed up close to its Tg. The ions radius ratio is about 1.24 between K^+/Cs^+ and 1.11 between K^+/Rb^+, which is lower than the ratio of 1.4 usually used in the soda-alumina-silicate glasses between Na^+ and K^+.

After a short time of ion exchange process below T_g, the glass remains transparent in the visible and the color of the glass surface changed from pale red to bright red. The color changes are function of heat-treatment time and temperature. Moreover, because of the large difference between the ionic radii of K^+ and Cs^+ ions, a large stress is introduced in the glass network which could provoke surface damages [16]. However, this phenomenon is less important for K^+/Rb^+ ion exchange. The obtained Cs^+ ion penetration depth measured with Energy Dispersive Spectroscopy analysis was compared to Rb+ for ion exchange performed at 310°C for several durations (figure 2).

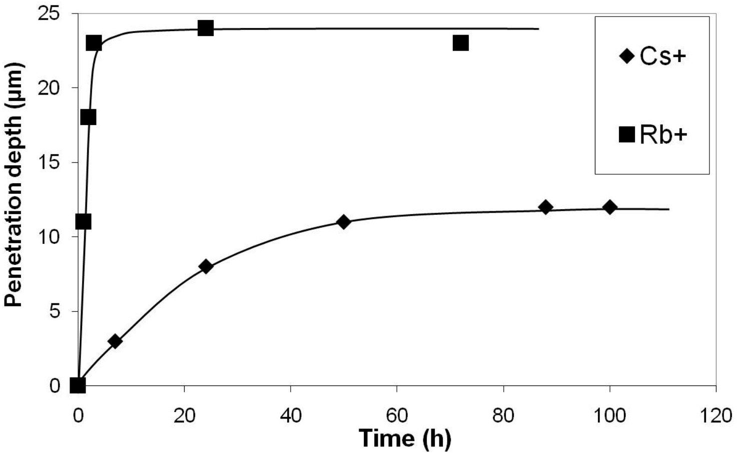

Figure 2. Penetration depth obtained with EDS Analysis of Cs+ and Rb+ in the 56GeSe$_2$-24Ga$_2$Se$_3$-20KI glass side after ion exchange at 310°C.

The other elements constituting the glass network such as Ge, Ga and Se do not diffuse in the molten salt bath, as their surface and bulk concentration do not evolve from the surface to the center of the glass. The effective diffusion coefficient of Cs^+ or Rb^+ ions can be calculated according to the formula [18]:

$$d=\sqrt{D_{eff}\tau} \qquad (1)$$

where d represents the ion exchange depth (µm), and τ represents the immersion time of the sample (h). According to the reached ion penetration depth, the maximum of the calculated effective diffusion coefficient D_{eff} for Cs^+ is about 2.1×10^{-5} µm²/s at 280°C, 5.2×10^{-4} µm²/s at 310 °C, and about 5.33×10^{-2} µm²/s at 310 °C for the Rb^+, for 3 hours of experiment. These results agree with the results presented by Jambon et al. demonstrating that the alkaline diffusivity is dependent of the ionic radius [13]. The large radius difference between K^+ and Cs^+ explains the smaller effective diffusion coefficient of Cs^+.

D has a temperature dependency according to the expression below:

$$D = D_0 \exp(-\frac{Q}{RT}) \qquad (2)$$

where D is the effective diffusion coefficient, D_0 is the pre-exponential term, Q is activation energy of effective diffusion, R is the molar gas constant, and T is the absolute temperature. According to the previous equation, the temperature increase of the molten salt leads to an accelerated diffusion. The relatively low T_g of our glass limited the use of broad range of temperature as in silicate glasses. In fact, it has been observed that the use of a high temperature, close to T_g, leads to the entire deterioration of surface by glass dissolution. Also, for a given temperature, the cations of smaller ionic radius diffuse more quickly. As a result, the immersion of glasses belonging to the GeSe$_2$-Ga$_2$Se$_3$-NaI system in NaNO$_3$/KNO$_3$ molten bath would permit to increase the penetration depth for a given time and to decrease surface mechanical stress by reducing the scales length and depth. However, only a small amount of NaI, not exceeding 20 % mol., can be incorporated in the Ge-Ga-Se base glasses. Thus, only glasses containing 10 % mol. are sufficiently resistant to crystallization to be used in ion exchange process.

Transmission curves of the 56GeSe$_2$-24Ga$_2$Se$_3$-20KI glass strongly evolve according to the immersion time and temperature. As observed in the figure 4, for short duration experiments at 310 °C, there are few transmission changes in the visible and in the infrared region. With increasing time, the maximum transmission of the sample strongly decreases and the glass becomes slowly opaque to visible light. The glass becomes totally opaque to infrared wavelength for ion exchange experiments longer than 150 h. Due to the higher effective diffusion coefficient of Rb^+ in the 56GeSe$_2$-24Ga$_2$Se$_3$-20KI glass, the transmission changes are observable at shorter times using the RbNO$_3$/KNO$_3$ molten bath than for Cs^+.

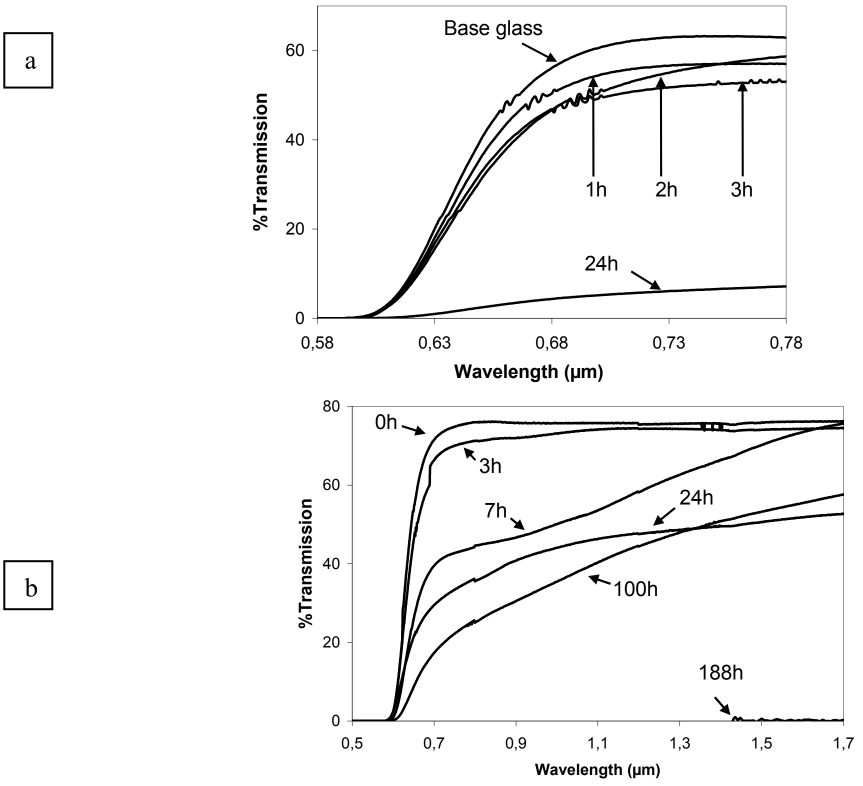

Figure 4. Transmission curves of the 56GeSe$_2$-24Ga$_2$Se$_3$-20KI glass composition after the ion exchange at 310°C for different durations in the RbNO$_3$/KNO$_3$ (a) and in the CsNO$_3$/KNO$_3$ (b).

As observable in figure 5, the use of bath containing oxygen and nitrate leads to new absorption bands, characteristic of oxide bonds phonon vibrations which appear at 7.2 µm, outside the 3-5 µm and 8-14µm atmospheric window. Furthermore, the Ge-O absorption band at 12.8µm increases according to the ion exchange time.

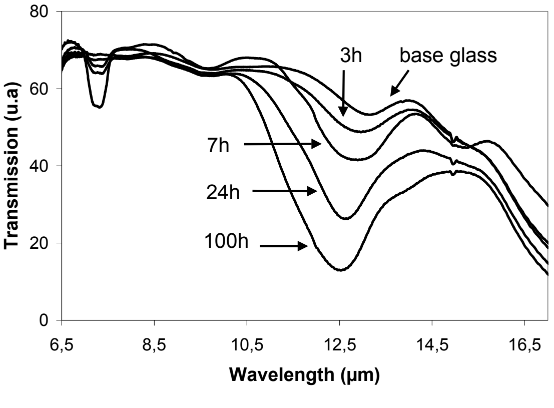

Figure 5. Infrared transmission curves of the 56GeSe$_2$-24Ga$_2$Se$_3$-20KI glass composition after ion exchange at 310°C for different durations in the CsNO$_3$/KNO$_3$.

Mechanical tests were performed on 56GeSe$_2$-24Ga$_2$Se$_3$-20KI glass slices of 20 mm diameter and 2 mm thick which were immersed in CsNO$_3$/KNO$_3$ and RbNO$_3$/KNO$_3$ molten baths at 310 °C for different times. The flexural strength σ_r has been calculated according to the following equation [19]:

$$\sigma_r = \frac{3P}{4\pi e^2}\left[2(1+\upsilon)\ln\frac{a}{b} + \frac{(1-\upsilon)(a^2-b^2)}{R^2}\right] \qquad (3)$$

with P : load (N), e : thickness (mm), a : radius of the load cylinder (18 mm), b : radius of the cylinder support (11 mm), R : glass diameter (20 mm), ν : Poisson's ratio.

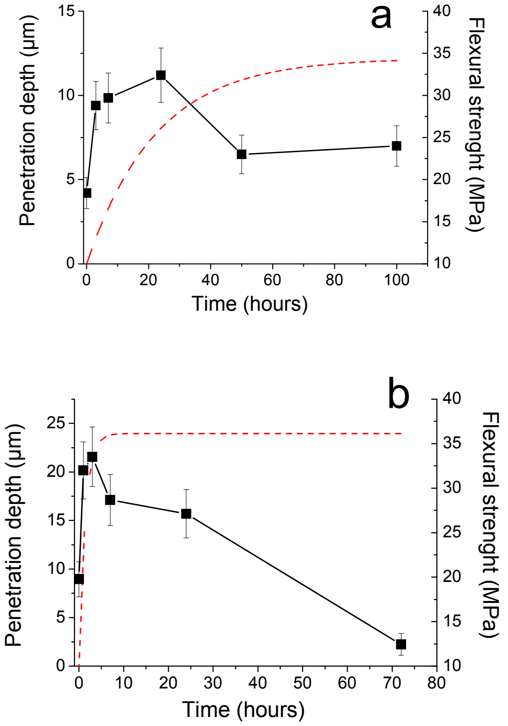

Figure 6. Flexural strength evolution in the $56GeSe_2$-$24Ga_2Se_3$-20KI glass according to ion exchange time at 310°C in the $CsNO_3/KNO_3$ (a) and in the $RbNO_3/KNO_3$ molten bath (b) and their respective penetration depth as a function of time is reminded with point segment.

The evolution of the flexural strength as a function of time is presented in figure 6. We can notice the progressive increase of the flexural strength with increasing penetration depth of Cs^+ or Rb^+ instead of K^+ up to a limit corresponding to the maximum penetration depth reached. For longer time, the strength of the chemically tempered glass falls down around the level of the untreated glass.

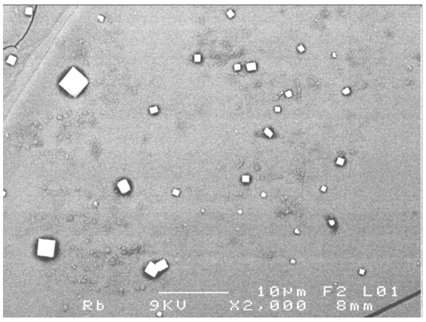

Figure 7. SEM pictures of the $56GeSe_2$-$24Ga_2Se_3$-20KI glass surface after 9 hours of immersion in a $RbNO_3/KNO_3$ molten bath.

In order to better understand the evolution of mechanical properties, the glass surface was observed more precisely by SEM and AFM on each treated sample. As observable in the figure 7, after long time of ion exchange (>24 h), small cubic crystals of RbI from 500 nm to 4 µm have been observed onto the glass surface, which tends to show that more than alkali exchange, a slight movement of halide must be considered. This phenomenon has not been observed with cesium. Furthermore, the glass surface roughness (Rq in nm) measured with AFM seems to be unchanged in the first step of the experiments and then quickly increases with ion exchange time, corresponding to the progressive glass sample degradation. Results are listed in table 2.

Table 2. Glass roughness (Rq in nm) measured with AFM according to the immersion time in $RbNO_3/KNO_3$ or $CsNO_3/KNO_3$ molten bath

	0 h	3 h	7 h	24 h
$RbNO_3/KNO_3$	7 ± 1 nm	7.3 ± 1 nm	38 ± 2 nm	Unmeasurable
$CsNO_3/KNO_3$	6 ± 1 nm	6 ± 1 nm	13 ± 1 nm	98 ± 2 nm

4. DISCUSSION

Contrary to soda-alumina-silicate glasses, the weak resistance of chalcogenide and chalco-halide glasses due to lower energy bonds, impedes to perform ion exchange between high radii ratio of ions without quickly damaging the surface. In fact, a small amount of ion exchange induces stress on the surface and provokes the appearance of flakes. The higher flexural strength can be explained by the compression phenomena created in deeper layers when Cs^+ and Rb+ are exchanged for controlled time in the glassy matrix. While the appearance of few flakes on the surface should decrease the flexural strength, the creation of compression phenomena on the surface increases it. We assume that the evolution of flexural strength in this glass is mainly linked to the shape of the bottom of the cracks. The experiments performed relatively closed to T_g induce a surface structural relaxation which can blunt the depth of the cracks inducing less critical damages. As demonstrated by Sane et al. [20], this phenomenon tends to reduce the surface stress, so that the maximum of compression is not at the surface but below it. However, for higher ion exchange time, the decrease of the flexural strength can be correlated to the whole degradation of the glass surface and to the increasing compression stress below the glass surface.

More than the movements of alkali into the glass surface, experiments have demonstrated that halide as iodine is not inert in the glassy matrix. However this ascertaining must be minimized as the phenomenon linked to halide movement starts with the glass surface degradation.

These results are a first approach to demonstrate the possibility to strengthen chalcogenide glasses using the ion exchange technique. Hence, the time/temperature parameters for Cs^+ and Rb^+ ion exchange must be adjusted to obtain the strengthening of the glass surface without damaging the transmission in the visible range.

Furthermore, the refractive index change according to the depth exchange could be used as an easy and economical method to produce waveguides in chalco-halide glasses.

4. CONCLUSIONS

In this paper, the efficiency of the ion exchange technique in selenium based chalco-halide glasses has been demonstrated for the first time. Experiments were performed on new Ge-Ga-Se-MX (MX: alkali halide) glasses, transparent from the visible range to the mid-infrared. The penetration depth reaches by Rb^+ and Cs^+ ions in the $56GeSe_2$-$24Ga_2Se_3$-20KI base glass were compared. A greater diffusion is observed by exchanging small radii ion and by using higher temperature. Furthermore, the incorporation of large cations such as Rb^+ and Cs^+ instead of smaller one introduced surface stresses. Consequently, small cracks are observed on the surface and the flexural strength has strongly increased for controlled time of ion exchange. The ion exchange between Rb^+ or Cs^+ and K^+ have led to a modification of the surface refractive index as the color of the glass surface change with increasing diffusion duration. These results can be considered as a first step to describe the complex ion exchange mechanism in these multi-component glasses to strengthen chalcogenide glasses. This technique can be a good alternative solution to chalco-halide glass-ceramics in order to improve mechanical properties. On the other hand, ion exchange could be an efficient technique in order to develop waveguide applications on different glass compositions.

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