Alkali aluminosilicate glasses and glass ceramics with improved mechanical properties

André Heitor Dinis
andre.heitor.dinis@tecnico.ulisboa.pt
Instituto Superior Técnico, Universidade de Lisboa, Portugal
July 2021

Abstract

Glass and glass ceramics based on alkali aluminosilicates (AAS) usually present excellent transparency and chemical durability. Ceramization of a lithium aluminosilicate glass composition was studied in order to obtain a transparent glass ceramic and study their mechanical properties. A thermal treatment of 575ºC, for 1h, yielded transparent glass ceramics with increased hardness of around 7% compared to as cast glass. The glass ceramics were then subjected to a chemical treatment in order to further enhance the mechanical properties, without hindering the optical transmittance. Vickers hardness, fracture toughness, fracture resistance and Weibull modulus were determined for polished glass, glass ceramic and ion exchanged (in KNO_3) samples. Combining heat treatment and chemical treatment (ion exchange at 450ºC 12h) resulted in a hardness increase of around 25%, from 620HV for the as cast glass, to 768HV upon both treatments. It was possible to conclude that a cumulative hardness increase phenomenon occurs with the combination of these two types of treatments. The fracture toughness values obtained with glass ceramic (1.6±0.1 MPa.$m^{0.5}$) were similar to those obtained for the cast glass but lower than those obtained for exchanged glass (2.2±0.1 MPa .$m^{0.5}$). The mechanical properties were optimized through the ion exchange treatment at 450ºC for 12h, unlike the heat treatment, which requires further study. However, it is possible to conclude that the AAS composition allows an optimization of the mechanical properties compared to a commercial glass studied (Gorilla Glass 5®).

***Keywords**: Alkali aluminosilicate glasses, glass ceramic, ion exchange, mechanical properties*

1 Introduction

Although glass is a material used since prehistory, its definition is not consensual within the scientific community. For example, according to Shelby[1] glass is an "amorphous solid completely devoid of long-range periodic atomic structure and with a glass transition region" and according to ASTM C162 a glass is "an inorganic product resulting from the fusion that is cooled under rigid conditions without crystallization occurring". Although these definitions reproduced here are not contradictory, they are complementary, and there is still no definition that fully characterizes this material[2].

In addition to the definition of glass not being completely closed, its properties make it difficult to classify it according to the three states of matter: solid, liquid and gas, since it has solid properties such as hardness, stiffness and brittleness but it also has properties, such as viscosity, of a supercooled liquid[2]. This caused a fourth state of matter to be considered: the vitreous state, where glass obviously fits[3]. In fact, any material with a glass transition temperature can be considered as vitreous. The glass transition temperature is a temperature at which the material can undergo a reversible change from solid to liquid, and is therefore a metastable state[4].

A new type of glass was discovered by Stanley Donald Stookey in 1953, glass ceramic. Also in this case, the definition has evolved and it is currently considered possible to consider a glass ceramic as a "ceramic material formed through the controlled nucleation and crystallization of glass[5]. The production process of glass ceramic begins by being the same as that of glass, but after the pouring and solidification it undergoes a thermal process called ceramization that promotes the internal crystallization of the glass[5].

The composition of the glass strongly influences its properties[5]. For the formation of glass ceramic it may be necessary to add nucleating compounds to the composition that will initiate nucleation in the crystallization process.

The present study is based on a previously developed lithium aluminosilicate glass composition[6] in which the aim was to optimize the mechanical properties of glass by an ion exchange process in KNO_3. Starting from the same vitreous composition, a ceramization treatment of the glass and a subsequent study of the effect of ion exchange on glass ceramic was carried out, in order to assess whether it is a cumulative effect (increase in hardness derived from ceramization and increase in hardness derived from ion exchange), allowing a compromise between mechanical and optical properties. A comparison of the results between glass, glass ceramic, exchanged glass and exchanged glass ceramic will be presented. Finally, the results will be compared with the results obtained for Gorilla Glass 5®, one of the most sold commercial glasses for mobile phone screens, tested under similar conditions.

2 Experimental method

The chemical composition of the starting material of this study, an alkali aluminosilicate (AAS - Alkali Aluminosilicate) is shown in Table 1.

Table 1: Composition, in weight (%) of AAS glasses

%	SiO_2	Al_2O_3	Li_2CO_3	MgO	ZnO	TiO_2	ZrO_2
	[62-69]	[10-16]	[7-11]	< 6	< 6	< 6	< 3

2.1 AAS glass preparation

After mixing the constituents indicated in Table 1, they are melted in a platinum crucible and then poured for the production of samples to carry out the intended tests, through the heating cycle shown in Figure 1 (red line). The various stages of heating aim to promote reactions between the constituents, namely at 900ºC to promote the decarbonation of lithium carbonate (Li_2CO_3). These compositions melt at approximately 1500ºC but its pouring was carried out at 1620ºC so that the melt has an adequate viscosity for pouring.

After the pouring of the glass samples, they are annealed with the purpose of relieving the stresses induced in the pouring. The corresponding heating and cooling cycle is shown in Figure 1 (yellow line).

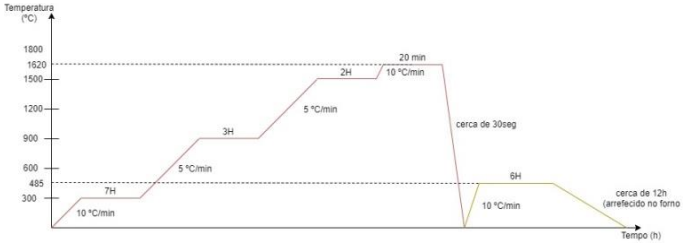


Figure 1: Furnace heating cycle for melting (blue line) and annealing (yellow line)

The samples were then CNC polished to a thickness of 1.2mm. Table 2 presents the roughness, determined by AFM, for CNC polished and manually polished samples.

Table 2: Roughness results of CNC polished and manually polished samples

	R_a [nm]	R_z [nm]
AAS CNC polished	$0{,}59 \pm 0{,}21$	$12{,}25 \pm 9{,}57$
AAS manually polished	$3{,}05 \pm 0{,}65$	$85{,}53 \pm 8{,}61$

2.2 AAS glass ceramic synthesis

After synthesis and characterization of the AAS glass, its ceramization was carried out through heat treatments performed between 570 and 580 ºC during 1h. These heat treatment conditions were chosen to maintain high transparency while increasing the hardness of the heat treated samples.

2.3 AAS glass ceramic ion exchanged synthesis

The definition of the most suitable conditions for ion exchange in AAS glass, with optimization of mechanical properties and maintenance of optical properties was carried out in a previous work[6]. As the starting composition used in this work is the same, the best results previously obtained were used as a starting point. Thus combinations between temperature (420ºC and 450ºC) and ion exchange time (9h, 12h e 30h) were studied in ceramic AAS glasses using the same experimental procedure.

2.4 Sample characterization

2.4.1 Density

Density measurements were done before and after the treatments carried out on the glass (thermal treatment and ion exchange) in order to monitor the possible alteration of this property. The measurements were carried out using the *Mettler Toledo AM50* scale, with its own assembly for the determination of density using Archimedes' principle. Measurements were performed with distilled water and the temperature was monitored during measurements.

2.4.2 UV-Vis transmission

These spectra were also measured before and after the treatments carried out on the glass (thermal treatment and ion exchange). They were performed on a Thermo Fisher Scientific Helios Gamma UV-Vis instrument. Measurements were taken between 190nm and 1100nm, with a resolution of 2nm.

2.4.3 X-ray diffraction (XRD)

Several XRD analyzes were carried out in order to characterize each type of glass (AAS as cast, AAS glass ceramic and AAS glass ceramic exchanged at 450ºC 30h). These analyses were performed in bulk samples on a *Bruker's D8 advance* equipment with the following experimental parameters: 2θ angles from 10 to 80, with step size 0.03 and step time of 1s, and with the samples rotating at 30RPM.

2.4.4 Elastic Constants

The measurement of elastic constants (Young's modulus, shear modulus and Poisson's coefficient) was done simultaneously, resulting from the output of the professional RFDA equipment from *IMCE nv*, through acoustic methods and in accordance with standard E1876-01[7]. These measurements were performed on CNC polished samples before heat treatment, after ceramization (575ºC-1h) and after ion exchange (conditions defined in chapter 5) to characterize the AAS samples.

2.4.5 Hardness

Hardness measurements were performed using Vickers microhardness in Struers Duramin equipment with application

of 200 grams for 15 seconds, before and after glass treatments.

2.4.6 Fracture toughness

Fracture toughness was estimated based on hardness measurements made using the Indentation-Fracture Method and was carried out in accordance with the JIS R 1607 standard[8]. To obtain these results, Mitutoyo's AVK-C2 durometer was used with loads of 5kg, 10kg, 20kg and 30kg and loading times of 15sec, 20sec and 25sec. These measurements were carried out before and after the treatments in order to monitor the mechanical properties of the glass throughout the various phases and estimate the fracture strength.

2.4.7 Fracture strength

To assess fracture strength, a ring-on-ring assembly (with support diameter equal to 20.2mm and load diameter equal to 10.1mm) was performed on an INSTRON 5566 loading machine with a traverse speed of 5mm/minute. These tests were carried out to characterize the three treatment phases (AAS as cast, AAS glass ceramic and AAS permuted glass ceramic) and the results were analyzed according to Weibull statistics. These tests were performed according with ASTM C1499-05 standard[9].

3 Results

3.1 AAS glass

AAS glass is the as cast glass, having not undergone any thermal or chemical treatment, serving as the starting point for the remaining results.

In order to determine the characteristic temperatures of this composition, a Differential Scanning Calorimetry (DSC) test was carried out, which allows the determination, among other things, of the glass transition temperature (T_g) and the melting temperature (T_f). This test can be performed with the bulk or powdered samples, and the result for both methods is quite similar (Figure 2), it can be observed that the glass transition temperature occurs at about 525ºC. This result will be important for the definition of annealing, heat treatment and ion exchange temperatures.

AAS glass was fully characterized and the summary of these results is shown in Table 3.

Table 3: AAS glass characterization results

ρ [g/cm³]	T [%] (700-750nm)	HV_{02}	E [GPa]	G [GPa]	ν	K_{IC} [MPa.m$^{1/2}$]
2,49 ±0,01	92	620 ± 8	87 ± 1	35 ±1	0,23 ± 1	1,7 ± 0,1

$\sigma_{rupture}$ [MPa]	Weibull modulus	c [µm]
308 ± 85	4,28	14,10

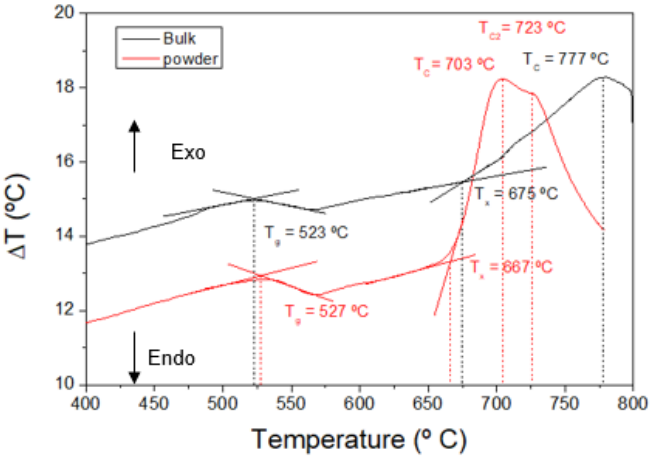


Figure 2: Result of DSC analysis of AAS glass[6]

3.2 AAS glass ceramic

The AAS glass ceramic underwent a thermal treatment of ceramization at 575ºC for 1h. This treatment aimed to promote crystal nucleation in the amorphous structure of AAS glass in order to study the evolution of hardness and other mechanical properties, but without compromising the optical properties.

All samples that were later subjected to ion exchange underwent heat treatment, which allowed monitoring the evolution of hardness, transmission and density to draw conclusions about the effect of heat treatment on these properties. This monitoring is found in Table 5 where the characterization results are indicated, as well as the variation that the properties suffered before and after the thermal treatment (TT).

AAS glass ceramic was fully characterized, and the summary of these results is shown in Table 4.

Table 4: AAS glass ceramic characterization results

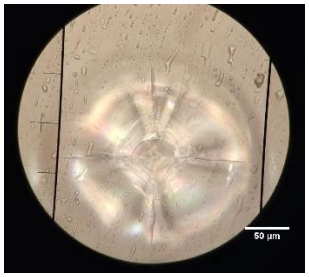
ρ [g/cm³]	T [%] (700-750nm)	HV_{02}	E [GPa]	G [GPa]	ν	K_{IC} [MPa.m$^{1/2}$]
2,46 ±0,01	92	679 ± 14	85 ± 1	34 ±1	0,24 ± 1	1,6 ± 0,1

$\sigma_{rupture}$ [MPa]	Weibull modulus	c [µm]
201 ± 92	2,89	29,32

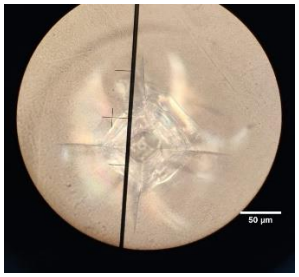
3.3 AAS glass ceramic ion exchanged

After TT the samples were subjected to ion exchange in KNO_3 (potassium nitrate). In order to optimize the ion exchange parameters (ion exchange time and temperature) to obtain the best match between mechanical properties and optical properties, the best results obtained in ion exchange on AAS glass were used: 9h, 12h and 30h at 420ºC and 450ºC[6].

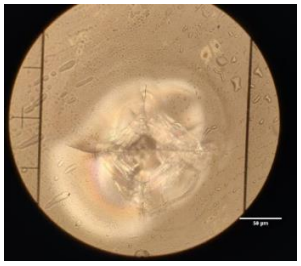
The results of the characterization of the ceramic AAS glass samples subjected to ion exchange, which are essential for determining the best conditions for optimization: hardness and transmission were monitored. Density and mass were also monitored, but their variation is residual. For each time-temperature pair, at least 2 samples were tested and the results presented are the average of the characterization of these samples.



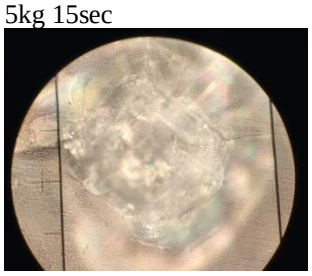
a) AAS glass with 5kg 15sec



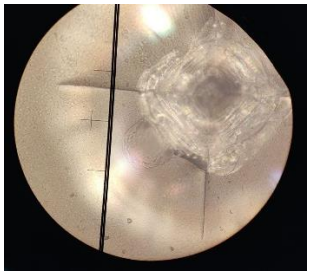
b) Ceramic AAS glass with 5kg 15sec



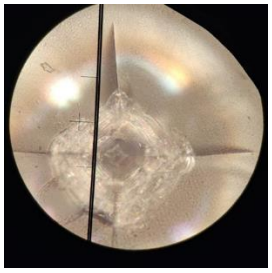
c) Ceramic AAS glass exchanged (420ºC 9h) with 5kg 20sec



d) Ceramic AAS glass exchanged (420ºC 12h) with 10kg 15sec



e) Ceramic AAS glass exchanged (450ºC 12h) with 10kg 15sec (half the indentation)



f) Ceramic AAS glass exchanged (450ºC 12h) with 10kg 15sec (half the indentation)

Figure 3: Several examples of indentations produced for K_{IC} measurement

In order to estimate mechanical properties such as fracture strength and crack propagation, several fracture toughness tests (K_{IC}) were performed, varying the load and time of its application for the applied load for the measurement of toughness in glass ceramic it was not possible to measure the cracks generated due to its small dimensions, which allows us to conclude that the ion exchanged AAS glass ceramic should have better mechanical properties than the AAS, ceramic AAS and even exchanged AAS glass. Figure 3 presents images of the indentations produced elucidating the impossibility of measurements in some cases, as in Figure c) and d). In figures e) and f) it is the same indentation but due to its dimensions two photographs must be taken in order to carry out the measurements.

Ion exchanged AAS glass ceramic was also characterized, and the results are summarized in Table5.

Table 5: Characterization results of the AAS glass ceramic ion exchanged samples

P [g/cm³]	T [%] (700-750nm)	HV_{02}	E [GPa]	G [GPa]	ν	K_{IC} [MPa.m$^{1/2}$]
2,46 ±0,01	86	773 ± 23	86 ± 1	35 ±1	0,23 ± 1	1,9 ± 0,1

$\sigma_{rupture}$ [MPa]	Weibull modulus	a [µm]
362 ± 84	4,94	12,75

3.4 Gorilla Glass 5®

As in the previously work[6], it is also important to establish a comparison between the results obtained by the AAS glass either after the cast or after the treatments induced, in order to frame these results with the commercial offer available, namely Gorilla Glass 5®, which is one of the most commercialized types of glass for smartphone screens.

These glass samples were subjected to the same characterization methods in order to make a direct comparison of results and those results are shown in Table 6. Note that as these glasses were industrially produced there were some tests that were done by sampling (not all the samples were tested).

Table 6: Gorilla Glass 5® glass characterization results

P [g/cm³]	T [%] (700-750nm)	HV_{02}	E [GPa]	G [GPa]	ν	K_{IC} [MPa.m$^{1/2}$]
2,42 ±0,01	96	579 ± 11	72 ±1	30 ±1	0,22 ±0	1,2 ± 0,1

$\sigma_{rupture}$ [MPa]	Weibull modulus	c [µm]
271 ± 97	3,11	9,07

4 Discussion

4.1 Glass ceramics synthesis

After performing several preliminary tests, it was verified that the heat treatment that produced a good compromise of optimization between the hardness and transmission in the visible was a heat treatment at 575ºC for 1h, as depicted from Table 7 and Figure 4. Although the 580ºC-1h combination presents better hardness results, its transmission is clearly

compromised and therefore cannot be considered in this study. The transmission results of 570ºC were not shown because they are very similar to those of 575ºC, but it presents lower hardness (11HV). Samples thickness is 1,2mm.

Table 7: Hardness evolution in the various experiment conditions

Conditions for heat treatment	Hardness (HV)
AAS	620 ± 8
570ºC 1h	668 ± 12
575ºC 1h	679 ± 14
580ºC 1h	719 ± 13

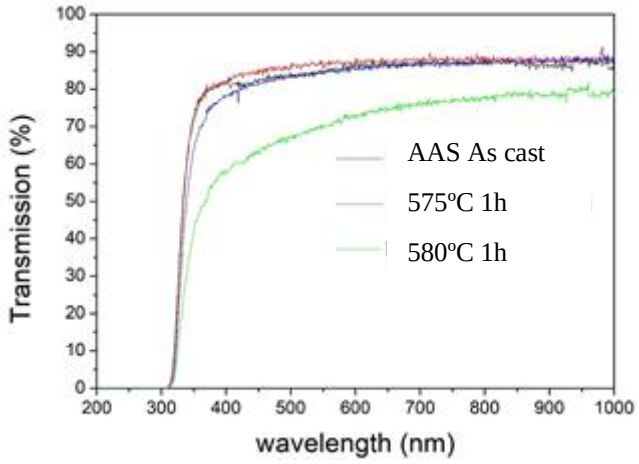


Figure 4: Transmission evolution in the various experiment conditions

4.2 UV-Vis transmission

The transmission of samples is one of the properties that needs greater control throughout the heat treatments carried out.

Through Figure 5, it is possible to see that the treatments performed do not significantly impact the transmission results. The heat treatment process could decrease the transmission of the samples as the crystallization of the samples causes them to become increasingly opaque, because ceramization involves nucleation (very abundant) but also crystal growth. If the average crystal size is less than or equal to 50nm, this will not affect transparency. Regarding the ion exchange process, it was already concluded in the previous work[6] that this chemical treatment does not affect the transmission of the samples, and the same was also observed in the present work.

The variation observed in samples transmission between the result after the exchange (ion exchanged AAS glass ceramic) and the result before the heat treatment (AAS glass) it's quite residual and it can be explained by the handling of samples that introduces scratches and this results in a small reduction in transmission and cannot be directly attributed to the treatments carried out.

A comparison must also be made between the transmissions obtained by Gorilla Glass 5® glasses (industrially produced) and those obtained by AAS, AAS ceramic and AAS ceramic exchanged glasses. This comparison is shown in Figure 6 and allows us to conclude that the transmission achieved by commercial glasses is higher due to the fact that they are obtained by an industrial production, but the other glasses manage to fulfill the objective of the intended application with the transmission obtained. The same figure also shows the transmission results of the AAS glass exchanged only at 450ºC 12h and it is possible to conclude that there were no substantial changes regarding the transmission of the AAS glass ceramic exchanged under the same conditions. Gorilla samples thickness is 0,9mm and the thickness of the other is 1,2mm.

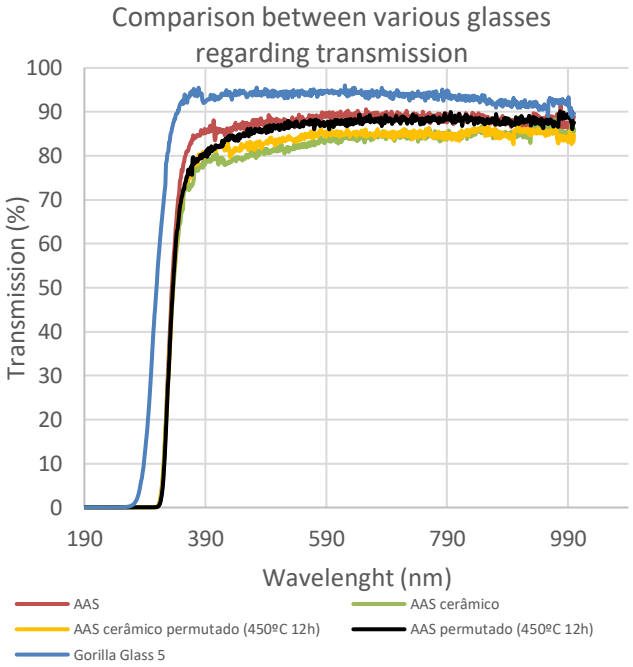


Figure 5: Comparison between various glasses regarding transmission

4.3 Hardness

In this study, the greatest attention is given to hardness since this, in conjunction with fracture toughness (K_{IC}), allows us to draw conclusions related to the effect of induced treatments on the glass and thus decide which time-temperature pair enhances its mechanical properties.

Table 8 shows the evolution of hardness over the various treatments applied to the glass and it is possible to conclude that there was a substantial increase in the hardness of the exchanged AAS glass ceramic compared to as cast AAS glass.

In Figure 7 it is possible to compare the hardness between various stages of the process: AAS, AAS exchanged at 420ºC and 450ºC, AAS ceramic, AAS ceramic exchanged at 420ºC and 450ºC and even Gorilla Glass 5®. After analyzing the graph, it is concluded that the hardness for the exchanged ceramic AAS glasses reached a peak at 12h at both temperatures, and then a decrease occurs, more accentuated for the higher temperature. On the other hand, the hardness of exchanged AAS glasses reaches a maximum at 450ºC in the same exchange time, but for exchange at 420ºC the peak is reached at 30h. The highest hardness is reached for exchanged ceramic AAS glasses and the hardness peak is reached for the 12h exchange. Thus, it can be concluded that the thermal and chemical treatments present cumulative results regarding hardness. It should also be noted that Gorilla Glass 5®, according to a patent published by its producer (Corning Glass)[10], is an aluminosilicate glass subject to ion exchange but its hardness is lower than that of as cast AAS glass.

Table 8: Evolution of hardness during treatments carried out on AAS glass

Ion exchange temperature (ºC)	Ion exchange time (h)	Before TT (%)	After TT (%)	After ion exchange (%)	Total variation (%)
420	9	620 ± 8	675 ± 16	720 ± 14	16,29
	12	620 ± 8	673 ± 13	763 ± 21	23,26
	30	620 ± 8	674 ± 15	745 ± 20	20,33
450	9	620 ± 8	692 ± 12	755 ± 20	21,78
	12	620 ± 8	693 ± 13	773 ± 23	24,84
	30	620 ± 8	672 ± 17	763 ± 23	23,06

The decrease in hardness, more accentuated at higher temperatures and/or longer ion exchange times, has already been studied by Erdem et al.[11] and is due to a viscoelastic relaxation phenomenon combined with a surface structural relaxation phenomenon. The viscoelastic relaxation phenomenon can be explained by equation (1) where ψ represents the expansion angle of the structure (which tends to zero with increasing temperature) and $\sigma_{core\ (t)}$ represents the tension of the core that increases with the factor $t^{1/2}$ and causes the surface compression to decrease[12].

$$\sigma(0,t) = \sigma_{core\ (t)} - \frac{kE}{1-v}\psi(t) \qquad (1)$$

Through the analysis of the Figure it is possible to conclude that the time/temperature pair that allows the greatest increase in hardness is 12h at 450ºC, but to make a decision this analysis must be complemented with an analysis of the results of fracture toughness (K_{IC}).

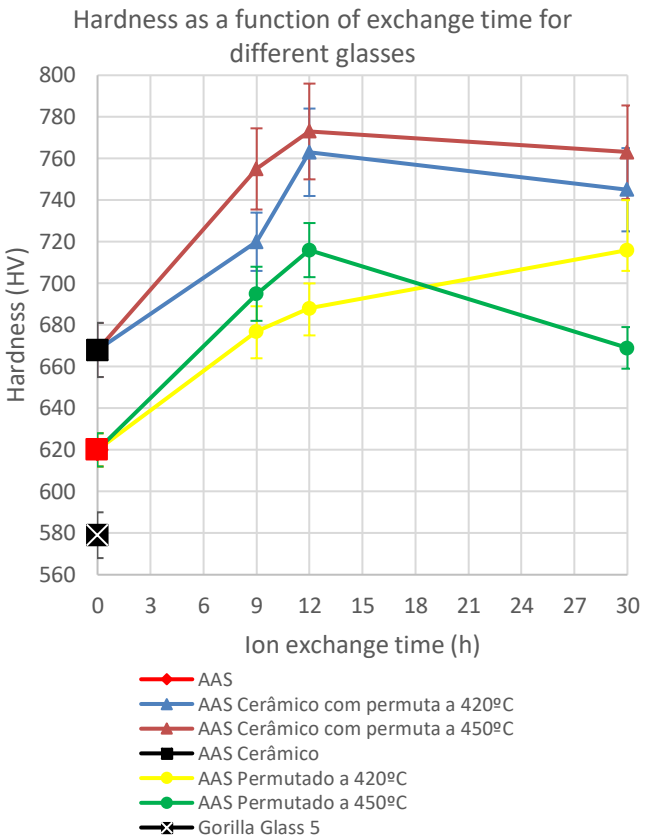


Figure 6: Hardness as a function of exchange time for different glasses

4.4 Fracture toughness

Contrary to what happened with the fracture toughness measurements of exchanged AAS glasses[6], in which measurements performed with 5kg for 15 seconds were able to produce indentations whose c/a ratio met the requirement required by JIS R 1607[8], in the case of permuted AAS glass ceramics this did not happen, so it was not possible to carry out a quantitative analysis but only a qualitative analysis of the indentations obtained, the more deformed and the larger the cracks, the worse the fracture toughness. According to JIR R 1607[8], the ratio between the cracks and the diagonals of the indentations should be greater than 2.5. To carry out this analysis, it was necessary to vary the loads and their application times between 10kg, 20kg and 30kg and 15sec, 20sec and 25sec, depending on the sample.

In Table 9 the "best" tests for each exchange condition are compiled. When performing this analysis, it is possible to conclude that ceramic samples exchanged at 450ºC will present better K_{IC} results. Among the samples treated at 450ºC, the 30h exchange should be excluded as it produces a more distorted indentation compared to the 9h and 12h exchanges at the same temperature. According with JIR R 1607[8] all the results presented, except those for 450ºC 12h, was where the 2,5 ratio was observed.

Table 9: "Best" K_{IC} tests for each exchange condition

Ion exchange conditions	Load and time	K_{IC}	c/a
420ºC 9h	5kg 20seg	3,18	1,86
420ºC 12h	5kg 20seg	3,08	1,80
420ºC 30h	5kg 20seg	2,60	2,12
450ºC 9h	5kg 20seg	3,40	1,64
450ºC 12h	10kg 15seg	1,86	3,08
450ºC 30h	Deformed indentations under any load and time		

Making a comparison between the K_{IC} obtained for ion exchange AAS glass ceramic (1,9 ± 0.1 MPa.m$^{1/2}$) and the K_{IC} measured for the various types of glass studied, it is possible to conclude that the exchanged AAS glass has a higher K_{IC} value (2.2 ± 0.1 MPa.m$^{1/2}$) since the thermal treatment on the glass increases the surface stresses, thus decreasing the K_{IC}, since the presence of crystals is not enough to prevent crack propagation. It is also important to mention that all AAS glasses, whether cast, exchanged or ceramic, have better fracture toughness values than commercial Gorilla Glass 5® glasses (1.2 ± 0.1 MPa.m$^{1/2}$), which means that this composition represents in itself an optimization of mechanical properties, as also verified in hardness.

4.5 X-ray diffraction (DRX)

The main function of the thermal treatment imposed on glasses is the production of a glass ceramic. In order to assess the crystallinity induced in the glass and still identify the phases present, X-ray diffraction (XRD) was used.

In Figure 7 is the compilation of all tests that were carried out in the three stages of the process: AAS (as cast), glass ceramic AAS (after being subjected to heat treatment) and even exchanged ceramic AAS (after ion exchange treatment), respectively. As you would expect, AAS glass is totally amorphous, AAS glass ceramic has a crystalline fraction, and exchanged AAS glass ceramic, although it has less crystalline fraction (less intense peaks), can still be considered ceramic.

Analyzing the database and the literature available for the composition used, it is possible to find two charts that may correspond to the phases present in the obtained diffractogram. As predicted in the literature, the beta-quartz and beta-spodumene phases are present in these glasses and it is still possible to have other phases with lesser expression, since the presence of nucleating agents introduces phases slightly different from those existing in literature charts.

The results of this analysis were affected by some experimental errors, and the error that affected the results, in this case, is the fact that the thickness of the samples analyzed was greater than that which should be used. This increase in thickness causes the sample not to be in the focus circle and thus the X-ray does not converge to the detector in the correct position which causes the peak to appear in an incorrect position in the diffractogram. This error can be corrected through algorithms, but since it is a systematic error, it is not mandatory to make a correction, it is only necessary to be aware of the reason for the deviation[13]. On an instrumental level, this error can be corrected through the use of parallel beam optics. These results are also somehow biased because it is not the same sample that undergo all the processes.

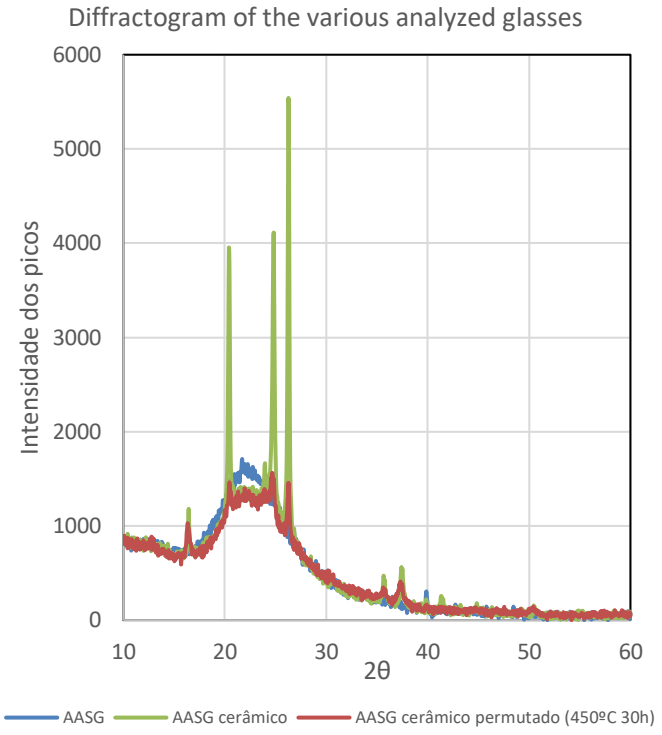


Figure 7: Diffractogram of the various analyzed glasses

Through the diffractograms it is also possible to obtain the crystalline percentage present in the glass ceramic and in the exchanged glass ceramic, through an empirical calculation, which results in indicative rather than absolute values. The reasoning used for this calculation was to calculate the area of the amorphous bump in the totally amorphous glass (AAS), which represents 100% amorphous and therefore 0% crystalline, and then calculate the area for the same bump in the diffractogram of the AAS glass. ceramic and the exchanged ceramic AAS and through an interpolation of these areas the amorphous percentage is obtained and, consequently, the crystalline percentage. Table 10 shows the values obtained for the crystalline and amorphous fractions of the aforementioned glasses, and it should be noted that the crystalline fraction decreased after ion exchange at high temperature (450°C) and long duration (30h) as the literature had described, in the phenomenon of crystal dissolution.

Table 10: Determination of crystalline and opaque fractions of various glasses

	Cristalline fraction	Amorphous fraction
AAS glass	0 %	100 %
AAS glass ceramic	8%	92%
Exchanged AAS glass ceramic at 450ºC 30h	3%	97%

- The fracture strength is higher in exchanged AAS glasses and the lowest fracture strength is recorded by glass ceramics, with a difference of 264 MPa between the mean values of the fracture strength recorded. The heat treatment introduces triaxial stresses which, together with the equibiaxial stresses induced in the ring-on-ring test, cause the fracture stress to decrease.

4.6 Comparison between glasses

Table 11 presents a compilation of all the results obtained for the studied glasses: AAS, exchanged AAS at 450ºC 12h, AAS glass ceramic, AAS ceramic exchanged at 450ºC 12h (Exchanged AAS ceramic) and Gorilla Glass 5® (GG5).

Looking through the different tests performed, it is possible to conclude that the density, transmission, and elastic constants (E; G; ν) are constant regardless of the treatment used, these values being used as a control for each glass used, since the fact that they are made individually can bring some inhomogeneities.

Through the remaining characterization, it is possible to observe the evolution of the properties of glasses during the treatments:

- Hardness is the property that undergoes a more evident evolution since there is a cumulative effect of increasing hardness with each treatment used, obtaining an increase of about 25% between AAS and AAS ion exchanged glass ceramic.
- Ion exchange improves the fracture toughness

5 Conclusions

Through the analysis of the characterization results of the studied glasses in this work, it is possible to conclude that the AAS composition glasses present better results than the studied commercial glass (Gorilla Glass 5®).

The XRD test confirmed the existence of crystalline phases in heat-treated glasses, with the main phases found being the β-quartz and β-spodumene phase, as predicted in the literature.

It was also concluded that the percentage of crystallinity in these glasses after the thermal treatment of 575°C-1h reaches 8%, decreasing to 3% after ion exchange, which indicates that the glasses have undergone crystal dissolution, a phenomenon also predicted in the literature for this type of glasses[14], [15].

Regarding hardness, both heat treatment and ion exchange (450ºC-12h), alone, mean an increase in hardness of around 7% and 13%, respectively. However, when the two treatments are combined there is a cumulative increase that represents an increase in hardness in the order of 25%, reaching a maximum of 773HV.

Table 11: Compilation of the studied glasses results

	P [g/cm^3]	Transm [%] (700-750nm)	HV_{02}	E [GPa]	G [GPa]	ν	K_{IC} [MPa.m$^{1/2}$]
AAS	2,49±0,01	92	620 ± 8	87 ± 1	35 ± 1	0,23 ± 1	1,7 ± 0,1
Exchanged AAS	2,49±0,01	81	716 ± 13	87 ± 1	35 ± 1	0,23 ± 1	2,2 ± 0,1
AAS glass ceramic	2,46±0,01	86	679 ± 14	85 ± 1	34 ± 1	0,24 ± 1	1,6 ± 0,1
Exchanged AAS cer.	2,46±0,01	86	773 ± 23	86 ± 1	35 ± 1	0,23 ± 1	1,9 ± 0,1
GG5	2,42±0,01	96	579 ± 11	72 ± 1	30 ± 1	0,22 ± 1	1,2 ± 0,1

	σ_{rutura} [MPa]	Módulo de Weibull	c [μm]
AAS	308 ± 85	4,28	14,10
Exchanged AAS	465 ± 172	2,47	10,36
AAS glass ceramic.	201 ± 92	2,89	29,32
Exchanged AAS cer.	362 ± 84	4,94	12,75
GG5	271 ± 97	3,11	9,07

Fracture toughness (K_{IC}) was not quantitatively evaluated in exchanged ceramic AAS glasses since, even after an increase in applied load and/or loading time, not enough cracks were generated to perform the measurement within the standard and in most cases the indentations were left unformatted, which prevents the correct reading of the values. Only one of the temperature-time pairs allowed the correct measurement of the cracks (within the parameterized in the standard), the ion exchange at 450ºC-12h, however its fracture toughness value is lower than that obtained for the AAS glass exchanged under the same conditions. It should also be noted that this property was reduced after heat treatment.

As for the mechanical properties, these are not properly optimized with the combination of thermal and chemical treatments since the best mechanical results, namely in the fracture tension, are obtained by glasses subjected "only" to ion exchange at 450ºC for 12h (average tension of 465MPa). A possible justification for the results obtained in AAS ion exchanged glass ceramics (average tension of 365MPa) is the introduction of triaxial stresses during the heat treatment that will cause these glasses to fracture at lower tensions, which is why AAS glass ceramic is the glass that obtains the lowest results among all those studied (average tension of 201 MPa).

It is possible to conclude that the AAS composition allows an optimization of the mechanical properties as it obtains better results than the commercial glasses analyzed. Ion exchange is the treatment that allows for greater optimization of mechanical properties. The thermal treatment of ceramization can allow an optimization of the mechanical properties, but it should be studied in more depth, since the higher the percentage of crystallinity, the greater the amount of induced triaxial stresses and the worse the mechanical properties obtained.

6 Future work

This study can be produced from the same composition with several other techniques in order to conclude whether or not they produce optimization of mechanical properties. A combination of treatments can also be considered, as reported in this work.

Among other techniques, the following are portrayed in the literature with promising results:

- Ionic implantation in glasses
- Double ion exchange with combination of KNO_3 and $NaNO_3$ in proportion
- Electric field assisted ion exchange

7 Acknowledgments

This work was supported by Fundação para a Ciência e Tecnologia (FCT), under the project *Glassmech - LISBOA-01-0145-FEDER-031192 | PTDC / CTM-CTM / 31192/2017*.

I thank my two supervisors, Professor Jorge Cruz Fernandes and Professor Luís Santos, for all their help and support throughout this year of research. I also thank Dr. Bruno Nunes and all the other researchers and laboratory technicians who helped me to obtain some essential results for this work.

8 References

[1] J. E. Shelby, *Introduction to Glass Science and Technology*, 2ª. 2005; Royal Society of Chemistry.

[2] M. Hasanuzzaman, A. Rafferty, M. Sajjia, and A.-G. Olabi, "Properties of Glass Materials," in *Reference Module in Materials Science and Materials Engineering.*, 2016, pp. 1–12.

[3] R. H. Brill, "A note on the scientist's definition of glass," *J. Glass Stud.*, vol. 4, pp. 127–138, 1962.

[4] A. I. Popov, "What is glass?," *J. Non-Crystalline Solids.*, 2018.

[5] M. Allix *et al.*, "Updated definition of glass-ceramics," *J. Non. Cryst. Solids*, 2018.

[6] I. Pinho, "Otimização das propriedades mecânicas de vidros aluminosilicatos alcalinos através de tratamentos químicos," 2021; tese de mestrado, IST/UL.

[7] ASTM, *E 1876-01: Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio by Impulse Excitation of Vibration*. 2001.

[8] "JIS R 1607: Testing methods for fracture toughness of high performance ceramics," *Japanese Ind. Stand.*, pp. 1–13, 1990.

[9] ASTM, *ASTM C1499-05, Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature*. 2005.

[10] C. Incorporated, "Patent US 9,387,651 B2: Methods for producing ion exchanged glass and resulting apparatus," 2016.

[11] I. Erdem, D. Guldiren, and S. Aydin, "Chemical tempering of soda lime silicate glasses by ion exchange process for the improvement of surface and bulk mechanical strength," *J. NonCrystalline Solids*, vol. 491, pp. 79–88, 2018.

[12] R. Gy, "Ion exchange for glass strengthening," *Mater. Sci. Eng.*, vol. 149(2), pp. 159–165, 2008.

[13] S. A. Speakman, "Basics of X-Ray Powder Diffraction," *Train. to Become an Indep. User X-Ray SEF Cent. Mater. Sci. Eng. MIT*.

[14] D. Tagantsev, "Decrystallization of glass-ceramics under ion exchange diffusion," *J. Eur. Ceram. Soc.*, vol. 19 (6–7), pp. 1555–1558, 1999.

[15] D. K. Tagantsev and G. O. Karapetyan, "Decrystallization of crystallized glasses by ion exchange," *J. Non. Cryst. Solids*, vol. 255(2–3), pp. 185–192, 1999.