

Double strengthening by ion exchange of sintered nepheline glass-ceramics: a new simplified method

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The possibility of achieving very high compressive stresses at the surface of nepheline glass-ceramics, owing to the transformation of main crystal phase into kalsilite, was discovered more than 40 years ago, but the very long processing times associated to conventional glass-ceramic manufacturing prevented extensive applications. The present work aims, on one hand, to explore the feasibility of nepheline-containing glass-ceramics by rapid sintering of fine glass powders and, on the other hand, to renew interest on strengthening by ion exchange induced transformation. For a selected glass-ceramic, developed using glass cullet as main raw material and sintered at very low temperature (840 °C), ion exchange treatments were found to be effective especially in increasing the reliability of samples (e.g. Weibull's modulus exceeding 18).

Key words: Fast sintering, X Ray Diffraction, Chemical tempering methods, Glass ceramics, Nepheline, Ion exchange, CRT Glass, Bending strength, Porous ceramics.

Introduction

Nepheline, i.e. NaAlSiO_4 or $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is known to be quite particular among the crystals developed upon controlled glass devitrification. Like in other feldspars and feldspathoids, Al^{3+} ions occur in tetrahedral coordination that is surrounded by four oxygen atoms. More precisely, the crystal is virtually identical to that of trydimite (form of crystalline silica), with part of $[\text{SiO}_4]$ units being replaced by $[\text{AlO}_4]$ units. Since the ions for the compensation of the charge neutrality are located in the interstitial sites, nepheline may be seen as a “stuffed derivative of silica” [1]. Within certain limits, sodium ions can be replaced by other “stuffing species”, such as potassium and calcium ions, thus forming nepheline solid solutions (with general formula $\text{K}_x\text{Na}_y\text{Ca}_z \square_{8-(x+y+z)}\text{Al}_{x+y+2z}\text{Si}_{6-(x+y+2z)}\text{O}_{32}$), where $\square$ represents a vacant cation site) [2].

The pioneering paper by Duke *et al.* [2] in 1967 revealed the possibility of exploiting the structure of nepheline for a remarkable chemical strengthening effect, based on the exchange of Na^+ with K^+ , applied to glass-ceramics. Unlike glasses, the high compressive stress at the surfaces is not simply due to the difference in ionic radius between sodium and potassium, but it is associated to a specific change in the crystal structure. As previously mentioned, potassium solubility in nepheline is limited,

so that the progressive replacement of Na^+ with K^+ ions causes the transformation of nepheline into kalsilite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with volumetric expansion. The compressive stress generated by the transformation is so high that bending strength of nepheline glass-ceramic rods after treatment can exceed the impressive level of 200.000 psi, i.e. ~ 1.4 GPa. The major issue concerns the composition of the starting glass: it was observed that glasses with a relatively high potassium content lead to the most remarkable strengthening. The incorporation of potassium into a nepheline solid solution likely led to a somewhat more “spaced” crystal lattice compared to pure sodium-based nepheline, thus favoring ionic diffusion.

The investigation presented here was conceived in order to renew the interest towards nepheline glass-ceramics transformed by ionic exchange, checking the conditions for: i) simplified glass-ceramic manufacturing, based on sintering; ii) modified strengthening, with effects on the reliability rather than on the strength of glass-ceramics. In fact, glass-ceramics with only nepheline as crystalline phase were developed by extremely slow conventional nucleation/growth treatments (4 h at ~ 850 °C + 4 h at 1100 °C), aided by high content (> 7 wt%) of TiO_2 in the starting glasses, acting as nucleating agent [2]. The nepheline glass-ceramics here discussed refer to a much simplified process, i.e. sintering of fine glass powders. According to recent experiences, this approach may lead to very fast crystallization, even in the absence of nucleating agents [3]. The feasibility of sintering or, better, “sinter-crystallization”, could promote the manufacturing of components with complex

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geometries, including highly porous foams (e.g. obtained by the replica method, already successfully applied to sintered glass-ceramics [4]).

The second challenge concerns the refinement of the chemical strengthening process. The usual treatment on glass, e.g. with potassium replacing sodium ions, provides high compressive stresses with maximum intensity just at sample surface. Surface cracks can propagate at higher applied loads (i.e. tensile stresses actually tend to expand the cracks only if exceeding the pre-compression), but the variability of crack length causes variability of strength like in an untreated material. In the presence of an “engineered stress profile”, that is maximizing compressive stress at a certain depth beneath the surface, the reliability of glass can be impressively enhanced (cracks from the surface experience an increasing resistance to their propagation) [5-10]. The feasibility of a double chemical treatment on glass-ceramics with reversible nepheline-kalsilite transformation, to the authors’ knowledge, is discussed for the first time in the present paper; double treatments, in fact, have been applied only to leucite-based glass-ceramics used for dental applications and obtained by a much more complex treatment than simple pressure-less viscous flow sintering, and with different transformation mechanism [11, 12].

Experimental Procedure

In the present work, we referred to three glass compositions (E, F and Centura® in Table 1) known to yield nepheline-based glass-ceramics. E and F glasses correspond to the most effective compositions reported by Duke *et al.*, whereas Centura® is a commercial glass-ceramic manufactured by Corning [1]. The composition of a panel glass from dismantled cathode ray tubes (CRTs), nominally recyclable, but practically unused, due to the limited production of new CRTs, is reported in Table 1. The glass can be effectively treated as a “waste glass”, to be considered only for products substantially different from CRTs (“closed loop recycling”); in fact, this specific type of glass has been already considered for glass foams or in the formulation of glasses to be converted into glass-ceramics [4, 13, 14, 15].

As previously specified, a primary goal of the present work was a simplified processing, especially concerning the crystallization, based on sintering. This led us to consider E and F compositions, tailored to promote crystallization by conventional nucleation and growth, without TiO₂ (nucleating agent). In addition, since glass frits (powders) are used, the fining of glass is not needed; this means that also As₂O₃ (fining agent) can be avoided. The compositions N1 and N2, reported in Table 2, effectively feature the same weight balance of characteristic oxides (SiO₂, Al₂O₃, Na₂O, K₂O) present in E and F glasses, respectively, without other oxides. N3 was inspired by Centura, but with significant

Table 1. Chemical composition of three reference glasses [1, 2] for the production of nepheline-based glass-ceramics and of a reference waste glass.

Oxides	Contents (wt%)			
	E	F	Centura®	Panel glass from dismantled CRTs
SiO ₂	41.4	40.8	43.3	62.0
Al ₂ O ₃	31.2	31.2	29.8	3.2
Na ₂ O	11.7	10.4	14.0	8.4
K ₂ O	7.5	9.5	–	6.3
MgO	–	–	–	1.1
CaO	–	–	–	1.8
BaO	–	–	5.5	12.6
SrO	–	–	–	4.7
As ₂ O ₃	0.7	0.7	0.9	–
TiO ₂	7.4	7.4	6.5	–

changes: again, TiO₂ was avoided in the glass formulation and, although the overall molar content of alkali oxides is almost the same, N3 features potassium oxide, absent in Centura. While N1 and N2 glasses were produced from pure oxides and carbonates, N3 was mostly derived from the CRT panel glass (64 wt%). N1 and N2 glasses were prepared by melting the raw materials at 1600 °C for 2 h in alumina crucibles; the two glasses, after rapid cooling by direct extraction from the furnace, were separated from the refractory crucible by cutting after the complete solidification. N3 glass was prepared by melting the raw materials at 1550 °C for 2 h in a Pt crucible; very rapid cooling was performed by pouring the glass melt in water.

Differential thermal analysis (DTA), (STA409, Netzsch Gerätebau GmbH, Selb, Germany) was performed with a 10 °C/min heating rate on fine glass powder, obtained by ball milling and sieved below 37 µm in order to infer the characteristic temperatures (glass transition, crystallization temperature).

Sintering experiments were carried out on disc samples with diameter of about 30 mm and thickness of 2 mm and on bigger samples with dimensions of about 50 mm × 35 mm × 4 mm; the specimens were obtained by uni-axial pressing at 40 MPa of fine glass powders in a cylindrical or rectangular steel die. All sintering experiments were particularly rapid: the samples were either directly introduced in the oven at the maximum temperature (“direct heating”, DH) or subjected to heating rate in excess to 10 °C/min and the holding time at the selected firing temperature was generally not exceeding 1 h (“conventional heating”, CH).

The bulk density of the sintered glass-ceramics was measured by means of the Archimedes’ principle. The residual porosity was estimated by image analysis performed by using the ImageJ program package [16] on micrographs taken by Scanning Electron Microscopy (ESEM Quanta 200, FEI Company, Eindhoven, The Netherlands). The crystalline phases development was

Table 2. Chemical composition, formulation and characteristic temperatures of the investigated glasses.

Oxides	Content (wt.-%)		
	N1	N2	N3
SiO ₂	45.1	44.4	48.7
Al ₂ O ₃	34.0	33.9	20.0
Na ₂ O	12.7	11.3	9.4
K ₂ O	8.2	10.4	9.0
MgO	–	–	0.7
CaO	–	–	1.1
BaO	–	–	8.1
SrO	–	–	3.0
64% CRT panel glass			
Formulation	Oxides and carbonates	Oxides and carbonates	9% SiO ₂ 18% Al ₂ O ₃ 4% Na ₂ CO ₃ 5% K ₂ CO ₃
T _g	760 °C	730 °C	600 °C
T _C	980 °C	1080 °C	840 °C

investigated by X-ray powder diffraction (Bruker AXS, D8 Advance, Karlsruhe, D) carried out with CuK α radiation (0.15418 nm) (in the 15–60 ° or 15–75 ° 2 θ range, with a step of 0.05 ° and scan time of 3 s) the diffraction patterns were analysed by Match! program package (Crystal Impact GbR, Bonn, D) [17], supported by data from the PDF-2 database (International Centre for Diffraction Data-ICDD, Newtown Square, PA). Additional X-ray diffraction measurements were performed on disc samples, without any treatment on the surface, in conditions of glancing-incidence (X-ray beam falling on a sample surface at a fixed angle of incidence-varying from 2 to 4 °-and diffraction profile recorded only by detector scan, with a step of 0.05 ° and scan time of 3 s).

Bending strength was determined on small beams of about 30 mm $\times$ 2 mm $\times$ 3 mm, cut from bigger samples. All beams were carefully polished to a 5 μ m finish and chamfered at the edges, by using diamond pastes. Four point bending tests (24 mm outer span, 8 mm inner span) were performed by using an Instron 1121 UTS (Instron, Danvers, MA), with a cross-head speed of 1 mm/min. At least ten samples per condition were considered.

A portion of the small beams were treated in molten KNO₃ and Na₂SO₄, at 590 °C. The samples and the salts were poured in a Pt crucible and heated with a rate of 10 °C/min; after a holding stage at 590 °C of variable duration, the crucible was subjected to natural cooling to room temperature and the samples were separated by washing in hot water. Selected samples were subjected to bending strength measurements after ionic exchange treatment. Also in this case, at least ten samples were considered for each condition.

Results and Discussion

Glass transition (T_g) and crystallization (T_C) temperatures of the three glasses are reported in Table 2. Fig.1 shows the evolution of bulk density as a function of the sintering treatment for N1 glass. The maximum density level is very close to that of the glass-ceramics prepared by Duke *et al.* [2], but it corresponds to a quite particular sintering condition, i.e. direct heating (DH) at high temperature. Sintering at the crystallization temperature, 980 °C, with a conventional heating rate of 10 °C/min (CH), determined visibly porous bodies, whereas quite smooth and brilliant surfaces were achieved at 1180 °C (T_C + 200 °C). The remarkable difference is likely due to intensive crystallization during conventional heating at temperatures below 980 °C; the formation of a number of rigid inclusions, corresponding to nepheline crystals, reasonably “froze” the viscous flow of the residual glass. The diffraction patterns shown in Fig. 2(a) confirm this hypothesis: the sample is substantially crystallized even for a very short holding time (30 min) at 980 °C, after conventional heating. The large specific surface of the fine glass powder evidently promotes the crystallization, even in the absence of nucleating agents, as observed for waste-derived glasses [3, 4, 15]. Direct heating at temperatures well exceeding T_C improves densification by changing the balance among viscous flow sintering and crystallization [3]: the glass, far above the transition temperature, experiences an enhanced viscous flow; the consequent reduction of free glass surfaces reduces the crystallization (see the limited intensity of the peaks in the pattern recorded on sample N1 treated at T_C + 200 °C for 1 h, pattern DH in Fig. 2(a)). The enhanced densification of samples “directly” sintered at 1180 °C, combined with partial crystallization, is evident in Fig. 3(a), showing isolated pores in a micro-crystalline matrix. Such evolution was accompanied by good mechanical properties, with the bending strength slightly exceeding 100 MPa, as reported in Table 3.

As demonstrated by the very close matching of powder diffraction peaks and reference lines in Figure 2(a), the developed crystal phase always corresponds to nepheline solid solution, Na₃K(Si_{0.56}Al_{0.44})₈O₁₆ (PDF#76-2465). The chemical composition is associated to substantial potassium incorporation (potassium and sodium ions being in the proportion 1 : 3), but also suggests the presence of vacancies (Si/Al ratio is higher than 1, thus determining an excess of positive charge, to be compensated by the “stuffing species”). Quite unexpectedly, the probable presence of vacancies did not help the transformation of nepheline into kalsilite upon the ion exchange treatment as reported by Duke *et al.* [2]. Glass-ceramics samples, prepared with the best sintering conditions (direct heating at 1180 °C,

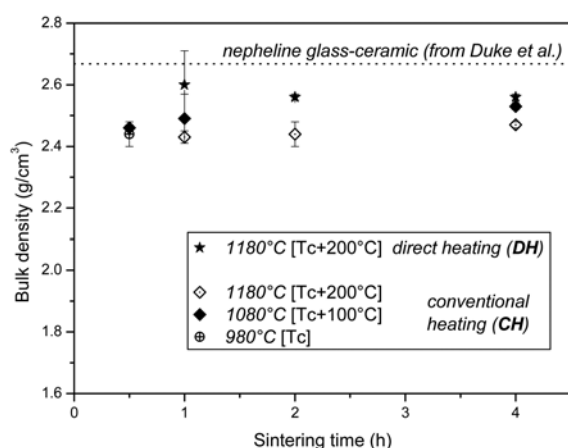


Fig. 1. Evolution of density with sintering treatments for N1 glass.

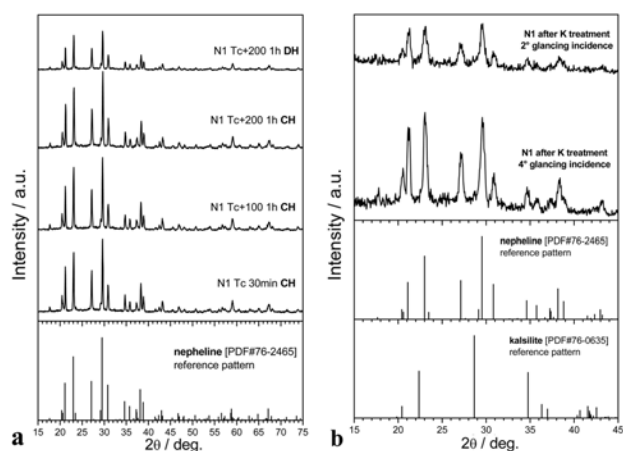


Fig. 2. a) phase evolution of N1 glass in different sintering conditions (powder diffraction-CH: conventional heating, DH: direct heating); b) glancing incidence x-ray diffraction pattern of N1 glass-ceramic after ion exchange treatment.

holding time = 1 h), broke into fragments during the treatment, initially scheduled to last 8 h (according to Duke *et al.* [2]). After a series of try-and-error tests, it was inferred that glass-ceramics from N1 glass could withstand a maximum of 2 h treatment in molten potassium nitrate.

The limited duration of the ion exchange treatment did not cause any appreciable change in the phase distribution on the surface, as shown by the glancing incidence diffraction analysis. Operating with a relatively high glancing incidence angle (4°, bottom pattern in Fig. 2(b)), i.e. collecting signals from the surface and from layers slightly below it (it is well known that patterns obtained at large glancing angles more bulk sensitive than those obtained at small glancing-angles) [18], the diffraction pattern reveals the same crystal phase found with powder analysis; operating with a lower angle (2°, top pattern in Fig. 2(b)), i.e. maximizing the contribution from the surface, the signals are obviously weaker, but with no practical change in the position of peaks. An effective transformation of nepheline should be accompanied by

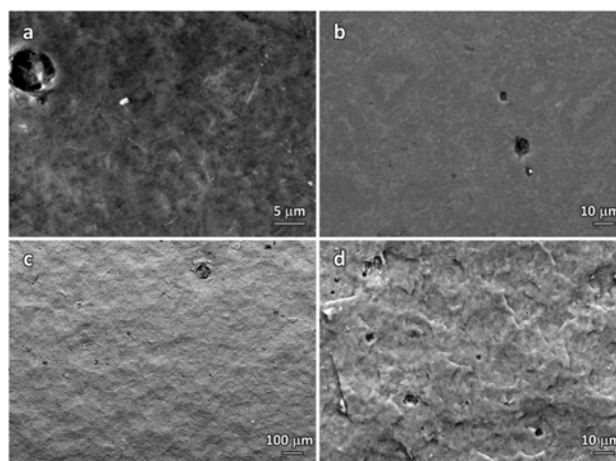


Fig. 3. Details of the surface of nepheline-based sintered glass-ceramics: a) N1; b) N2; c,d) N2 after ion exchange treatment.

the shift of some main peaks (e.g. those at $\sim 23^\circ$ and $\sim 30^\circ$) and the disappearance of others (e.g. that at $\sim 27^\circ$). The absence of surface changes is further confirmed by the strength values, which remain similar to those of as prepared N1 glass-ceramic (Table 3).

A quite different behavior was found for N2 glass. Based on a different balance among constituents, N2 glass features higher crystallization temperature (1080 °C) than N1 glass, but shows good densification at the same temperature (porosity slightly exceeding 2%) by direct sintering (see Fig. 3(b)). The previously presented nepheline solid solution, $\text{Na}_3\text{K}(\text{Si}_{0.56}\text{Al}_{0.44})_8\text{O}_{16}$, is confirmed as the characteristic crystal phase, as shown by Fig. 4. However, the glass-ceramic from N2 glass is weaker than the one from N1 glass (see Table 3), and exhibits a higher sensitivity to ion exchange. More precisely, glass-ceramic from N2, sintered at 1080 °C (for 1 h), was able to withstand the treatment in potassium nitrate for 3 h and undergo to some transformation, as shown in Fig. 4(b). The peaks corresponding to the main crystal phase, nepheline, are almost negligible compared to those corresponding to K-rich phases, such as kalsilite (KAlSiO_4 or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, PDF#76-0635) and leucite (KAlSi_2O_6 or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, PDF#85-1421).

The occurrence of the expected transformation of nepheline into kalsilite did not determine any strength improvement; conversely, as reported in Table 3, the bending strength decreased substantially (almost 40%). Fig. 3(c-d) show the changes occurring on the surface after ion exchange treatment; the surface, originally smooth (after cutting from larger specimens and polishing), become rougher after the treatment.

In our opinion the results from the ion exchange treatment of glass-ceramics from both N1 and N2 glasses differs only in terms of intensity. The expected volume increase, associated to the insertion of K^+ within the nepheline structure and its transformation into kalsilite, effectively occurred but it was not sustainable at the interface with the unmodified material. The

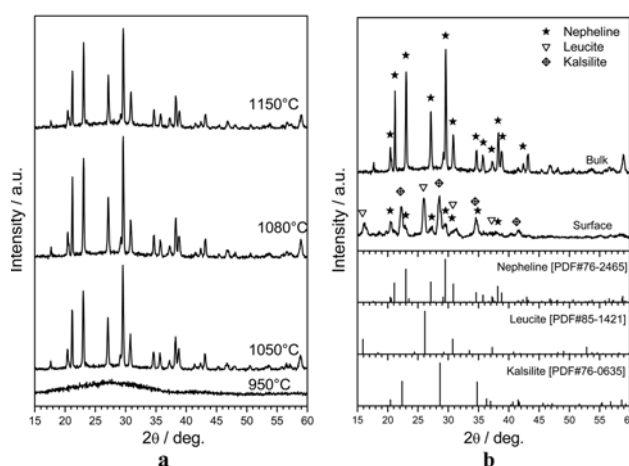


Fig. 4. a) phase evolution of N2 glass at different sintering temperatures (powder diffraction; holding time = 1 h); b) comparison between powder diffraction pattern (1080 °C, 1 h) and glancing incidence pattern after ionic exchange treatment (3 °).

mutual constraint of transformed crystals forced them to develop a significant interfacial stress, likely enhanced by the residual micropores (acting as stress concentrators). In other words, the strengthening observed by Duke *et al.* [2] is probably possible only with pore-free materials, difficult to be obtained by pressureless sintering.

The third glass, N3, was considered with the main aim of limiting nepheline formation. In fact, a reduction in the content of the crystal phase undergoing transformation was thought to “dilute” the stresses arising from the ion exchange treatment and to maintain the integrity of the samples. Fig. 5(a) clearly shows that leucite (PDF#85-1419) is formed together with nepheline after sinter-crystallization at 840 °C (1 h). The new formulation allowed a much lower processing temperature, without direct heating: the enhanced content of network modifiers (e.g. BaO and SrO), not to be incorporated in the crystal structure, favor viscous flow even at relatively low temperatures; crystallization can be coupled with a satisfactory densification (residual porosity of about 3.5%) even with finite heating rate (20 °C/min). The semi-quantitative phase analysis provided by the Match! program package suggests a 60/40 nepheline/leucite weight proportion; considering the composition of N3 glass, this would be associated to an approximate crystallization degree of 65%.

As reported in Table 3, the strength of nepheline-leucite glass-ceramics from N3 glass (approximately 70 MPa) is far below that of nepheline glass-ceramics from N1 and N2, but it increases sensibly after the ion exchange treatment in molten potassium nitrate without any degradation of the sample surface, as shown by Fig. 5(a).

The glancing incidence diffraction patterns of Fig. 6 show the occurrence of nepheline-to-kalsilite transformation,

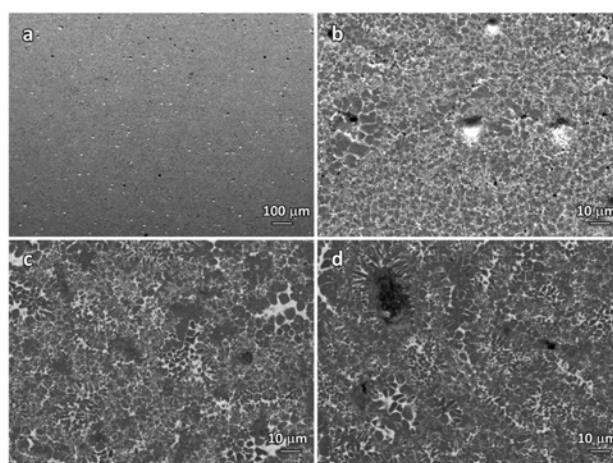


Fig. 5. Details of the surface of sintered glass-ceramics from N3 glass: a,b) after sintering; c) after first treatment, in molten K-nitrate; d) after second treatment, in molten Na-sulphate.

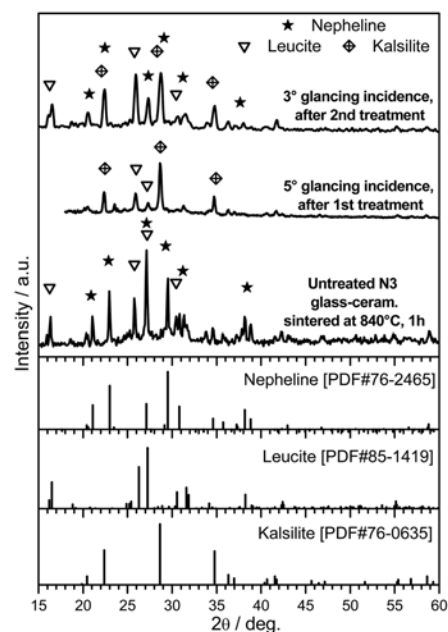


Fig. 6. Diffraction patterns of glass-ceramics from N3 glass, before ion exchange (powder analysis) and after ion exchange treatments (glancing incidence).

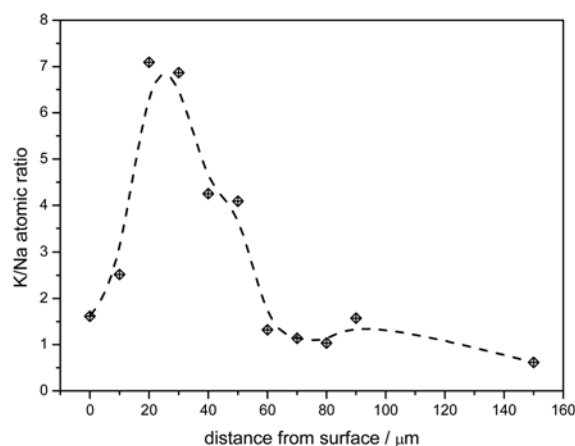


Fig. 7. Trend of K/Na ratio with increasing distance from the surface of a sample subjected to double ion exchange treatment.

Table 3. Sintering conditions, porosity and mechanical properties, before and after ion exchange treatments, of sintered glass-ceramics from the investigated glasses.

		N1	N2	N3
Optimal sintering temperature (°C)		1140	1080	840
Heating mode		Direct	Direct	20 °C/min
Density (g · cm ⁻³)		2.60 ± 0.11	2.56 ± 0.02	2.77 ± 0.1
Porosity (%)		2.1 ± 0.5	2.3 ± 0.8	3.4 ± 0.7
Mean value ± Std. Dev. (MPa)		102.7 ± 12.8	88.5 ± 11.6	73.0 ± 15.9
Bending strength	Weibull parameters:			79.8
	σ_0 (MPa)			4.9
	m			
Soaking time in molten K salt		2 h	3 h	8 h
Mean value ± Std. Dev. (MPa)		93.6 ± 35.0	56.5 ± 20.8	140.2 ± 12.4
Bending strength, after ion exchange (K)	Weibull parameters:			146.3
	σ_0 (MPa)			12.2
	m			
Soaking time in molten Na salt		–	–	4 h
Mean value ± Std. Dev. (MPa)				99.4 ± 5.40
Bending strength, after 2 nd ion exchange (K, Na)	Weibull parameters:			102.0
	σ_0 (MPa)			18.4
	m			

in N3 glass-ceramic, after 8 h in K-nitrate, and its reversibility, after additional 4 h in Na-sulphate. Nepheline, not recognizable in the pattern after the first treatment, is found again after the second treatment, along with leucite and kalsilite, according to sodium diffusion. The partial restoration of nepheline is testified by the distribution of potassium and sodium (determined by energy-dispersive x-ray spectroscopy (EDS) analysis) along the thickness of samples, as shown in Fig. 7.

Fig. 5 also testifies that glass-ceramics from N3 glass were subjected to a sort of “recrystallization” during ion exchange treatments. In fact, crystals change from a quite uniform distribution in untreated sample (Fig. 5 (b)) to an almost bimodal distribution, with larger crystals (diameter of about 5 µm) surrounded by smaller ones, in treated samples (Fig. 5(c-d)); the amorphous phase, clearly recognizable from the light coloration in backscattered images (associated to heavier elements, such as Ba and Sr), is also modified, being more concentrated in some points. This suggests an “active” role of the residual glass phase during the crystallization; a glass network with relatively larger free volume, due to large ions (again, Ba and Sr), likely promotes the diffusion of alkali ions.

The presence of a point of maximum potassium concentration below the surface (20–25 µm) (Fig. 7) can be correlated to a maximum compressive stress at that depth, as reported for an “engineered stress profile” (ESP) [5, 6, 10]. Like in ESP glass [6, 10] the main effect does not concern the level of strength (reduced at approximately 100 MPa), but the scatter of the data. As reported in Table 3 the standard deviation of strength is

well below 10% of the average level, and Weibull modulus exceeds 18.

A final remark concerns the possible impact of the proposed approach. To the authors’ opinion the strengthening and the dramatic decrease of dispersion of strength data could be an opportunity for glass-ceramic components loaded in bending, especially thinking at porous materials. As well discussed by Gibson and Ashby [19], the strength of open-celled foams is conditioned by the bending strength of the cell edges (“bending-dominated” behaviour); improvements in the bending strength of the solid phase could lead to an impressive strengthening of foams, to be variously exploited (construction of lightweight cores for sandwich structures, impact absorbers, filters etc.) [19]. The possibility to apply a sintering approach would greatly simplify the manufacturing of highly porous foams, as previously mentioned [4]. Finally, it should be observed that nepheline may be found as one of the main phases in waste-derived glass-ceramics [15, 20, 21]: the fabrication of high strength foams, after sintering and ionic exchange treatment, could allow high value applications for waste glasses.

Conclusions

Ion exchange-induced nepheline-kalsilite transformation has been observed in glass-ceramics produced by sintering sodium-potassium alumino-silicate glasses. The transformation could not be exploited for glass-ceramics with only nepheline as crystalline phase; the intense stresses developed upon ion exchange, combined with a limited but not negligible residual porosity, led to the

rupture of samples upon the chemical treatment. On the other hand, successful treatments were applied to nepheline-leucite glass-ceramics, obtained by re-using a significant content of waste glass. The reversibility of nepheline-kalsilite transformation was found to be suitable, more than for strengthening, for an impressive reduction of the scatter of strength data. This fact could find applications in the manufacturing of (especially porous) reliable glass-ceramics, where mechanical properties remain a critical point.

Acknowledgments

I.P. and E.B. thank Mr M. Capovilla for experimental assistance and EU for financial support in the framework of the European Project “GlaCERCo-ITN” (Glass and Ceramics for High Technology Applications-Initial Training Network, Marie Curie Actions-FP7, g.a. #264526).

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