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Low temperature sintering of fluorapatite glass-ceramics

Isabelle Denry and Julie A. Holloway

The University of Iowa College of Dentistry Department of Prosthodontics & Dows Institute for Dental Research Iowa City, Iowa, USA

Abstract

Fluorapatite glass-ceramics have been shown to be excellent candidates as scaffold materials for bone grafts, however, scaffold production by sintering is hindered by concurrent crystallization of the glass. Our goal was to investigate the effect of Ca/Al ratio on the sintering behavior of Nb-doped fluorapatite-based glasses in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-MgO-Na}_2\text{O-K}_2\text{O-CaO-CaF}_2$ system. Glass compositions with Ca/Al ratio of 1 (A), 2 (B), 4 (C) and 19 (D) were prepared by twice melting at 1525°C for 3h. Glasses were either cast as cylindrical ingots or ground into powders. Disc-shaped specimens were prepared by either sectioning from the ingots or powder-compacting in a mold, followed by heat treatment at temperatures ranging between 700 and 1050°C for 1h. The density was measured on both sintered specimens and heat treated discs as controls. The degree of sintering was determined from these measurements. XRD showed that fluorapatite crystallized in all glass-ceramics. A high degree of sintering was achieved at 775°C for glass-ceramic D ($98.99 \pm 0.04\%$), and 900°C for glass-ceramic C (91.31 ± 0.10). Glass-ceramics A or B were only partially sintered at 1000°C ($63.6 \pm 0.8\%$ and $74.1 \pm 1.5\%$, respectively). SEM revealed a unique microstructure of micron-sized spherulitic fluorapatite crystals in glass-ceramics C and D. Increasing the Ca/Al ratio promoted low temperature sintering of fluorapatite glass-ceramics, which are traditionally difficult to sinter.

Keywords

Glass-ceramics; fluorapatite; akermanite; crystallization; sintering

Introduction

Apatite-based glass-ceramics have long attracted interest as synthetic materials for bone replacement [1-5]. They are used in bulk form, powders, coatings, and more recently have been investigated as macroporous scaffolds [6]. The excellent biocompatibility of hydroxyapatite and fluorapatite glass-ceramics is classically related to their chemical and crystallographical similarities with the apatite phase present in bone [7]. Compared to bioinert ceramics such as alumina, the main potential advantage of apatite-based glass-ceramics is the formation of a chemical bond at the ceramic-bone interface [8, 9]. High resolution TEM studies have clearly demonstrated the formation of *de novo* apatite crystals by epitaxial growth on the surface of hydroxyapatite-containing ceramics [10]. Moreover,

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Corresponding Author: Isabelle Denry The University of Iowa College of Dentistry 801 Newton Road, Iowa City, IA 52242, USA
Phone: (319) 335-7369 Fax: (319) 335-8895 Isabelle-Denry@uiowa.edu.

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apatite crystallization in apatite-mullite glass-ceramics has been shown to elicit an excellent bone tissue response after implantation in rat femurs, while the corresponding amorphous glass induced an inflammatory response. [11] These findings raise the important issue of the role of topography and microstructural features in the pace of *in vivo* integration of apatite-based glass-ceramics and implant materials [12-14]. Meanwhile, our previous work has revealed that fluorapatite glass-ceramics doped with small amounts of niobium oxide crystallized into a very fine dual microstructure composed of submicrometer fluorapatite spherical crystals, together with forsterite polygonal crystals [15]. This microstructure is strongly influenced by the conditions of crystallization heat treatment, namely duration, temperature and cooling rate [16]. Further work revealed that the surface topography associated with this type of microstructure led to excellent attachment, proliferation and differentiation of human mesenchymal stem cells [17]. Recent investigations on the crystallization mechanisms of apatite-mullite glass-ceramics also demonstrated that control of crystal morphology to form arrays of apatite nanocrystals is achievable in this system, through modulations of the glass composition and heat treatment regime [18-20].

As mentioned earlier, bioactive glass-ceramics are available in various forms and shapes. The present work focuses on the preparation of fluorapatite glass-ceramics for the production of macroporous scaffolds. Inspired by progress in the fabrication of open-celled ceramics, several processing techniques have been developed to prepare macroporous ceramic scaffolds for bone replacement [21]. Amongst these techniques, one of the most common is the impregnation of an open-cell polymer foam with a ceramic slurry that is later dried and sintered while the polymeric template is eliminated [22]. This polymer foam impregnation technique is an attractive method for producing glass-ceramic scaffolds from bioactive compositions, including hydroxyapatite, fluorapatite and β -TCP-containing glass-ceramics [23]. However, hydroxyapatite and fluorapatite ceramics are traditionally difficult to sinter, even as mixtures of powders [24-26]. Low temperatures result in high porosity and incomplete sintering, while high temperatures in excess of 1000°C may lead to decomposition, loss of hydroxyls or fluorine and formation of pyrophosphates [27]. Additionally, in glass-ceramic systems, crystallization may occur during sintering and hinder the densification process [28, 29]. Indeed, it is well established that independently of the nature of the crystalline phases forming, chemical compositional changes in the remaining glassy matrix are likely to induce changes in viscosity, which in turn may prevent adequate sintering [30-32]. Concurrently, several studies have shown that adequate sintering is only possible if sintering precedes crystallization [31, 33]. One way to improve sinterability for a given composition is therefore to extend the working range to allow viscous flow sintering prior to crystallization. This can be done by fine-tuning the glass composition and replacing intermediate oxides such as alumina with alkaline-earth modifiers such as calcium oxide [34, 35]. Moreover, studies in multicomponent bioactive silicate glasses revealed that when introduced as calcium fluoride, and in the presence of phosphorous pentoxide, calcium causes a decrease in the glass transition temperature, together with an increase in the crystallization temperature, thereby efficiently increasing the processing window [36]. Calcium is also a key component in the development of bioactivity in bioactive glasses [37]. Meanwhile, aluminum oxide has been shown to be detrimental to the bioactivity of calcium silicate glasses [38-40]. The purpose of the present study was to investigate the effect of calcium to aluminum ratio on the sintering and crystallization behavior of fluorapatite glass-ceramics. The hypothesis tested was that increasing the amount of calcium oxide at the expense of aluminum oxide would increase sinterability by extending the processing range prior to crystallization of fluorapatite.

Materials and methods

Specimen preparation

Four glass compositions with increasing calcium to aluminum atomic ratio were prepared by mixing reagent grade oxides and carbonates (Table 1). Fluoride was introduced as calcium fluoride and was added in excess as 50% losses by volatilization were anticipated. Batch ingredients were melted at 1525°C for 3 h in platinum crucibles. After quenching in deionized water, the glass frits were powdered and melted again at 1525°C for 3 h. The molten glasses were cast to form cylindrical rods (10 mm in diameter; 60 mm in length). The rods were furnace-cooled from 685°C to room temperature and sectioned into disks (10 mm in diameter; 1 mm thick) using a low speed diamond saw. Specimens were heat treated in the temperature range 700-1050°C for one hour at a heating rate of 2°C per minute. Glass frits from the same compositions were prepared as described earlier. Frits were powdered and sieved to a particle size of 45 micrometers or less. Disk-shaped specimens (10 mm in diameter; 1 mm thick) were produced by uniaxial pressure using a polyvinylsiloxane mold. Specimens were sintered in air at temperatures ranging between 700 and 1050 °C for one hour.

Crystallization behavior

The crystallization behavior was investigated by differential scanning calorimetry (Q600 DSC/TGA, TA Instruments). Analyses were performed on glass frit particles placed in matched platinum-rhodium crucibles under nitrogen gas flow. Aluminum oxide powder (99.99%) served as a reference standard. First, the optimum nucleation temperature (ONT) was determined for each glass composition. This temperature is defined as the “temperature at which the most number of stable nuclei form per volume element” [18]. ONT was investigated by DSC after one hour nucleation holds at various temperatures, followed by full crystallization, according to the method proposed by Marotta *et al.* [41]. The ONT was determined as the hold temperature leading to the lowest temperature for the first crystallization exotherm. Further DSC experiments were conducted at heating rates of 10, 20, 30 and 40°C/min. on samples nucleated at the ONT. The activation energy of crystallization (E_C) for fluorapatite was calculated from the slope of the classical Kissinger plot, using the Kissinger equation [42]:

$$\frac{E_C}{RT_p} = \ln \left(\frac{T_p^2}{v} \right) \quad (1)$$

where T_p is the temperature of the crystallization exotherm and v is the heating rate.

The coefficient of thermal expansion and softening point were determined by dilatometry on glass bars sectioned from the cast ingots (Orton dilatometer, Model 1600D). Crystalline phases were characterized by X-ray diffraction on powdered and bulk specimens. Scans were performed in the two-theta range 10-60°, at a scanning rate of 1°C/min. (Miniflex II diffractometer, Rigaku Americas). Additionally, specimens sintered at 800°C/1h were analyzed at a scanning rate of 0.2 degrees per minute in the two theta range 3-90 degrees at 40kV and 44mA in Bragg-Brentano configuration (SmartLab, Rigaku Americas). Peak positions were determined using PDXL-2 analysis software (Rigaku Corporation) after calibration using silicon powder standard (NIST, 640d). The microstructure was investigated by scanning electron microscopy under secondary electron imaging (Hitachi S-4800 field emission SEM). Specimens were polished to a 0.5µm finish using as series of abrasives ending with diamond polishing pastes. They were etched with diluted hydrofluoric acid and gold coated prior to SEM examination. A variable pressure scanning electron microscope (VP-SEM, Model 3400, Hitachi High Technologies America, Inc.), coupled with a back-

scattered electron detector, was used to perform semi-quantitative Energy Dispersive Spectroscopic analyses on uncoated specimens. X-rays were detected at an accelerating voltage of 15 kV and a working distance of 10 mm (Bruker AXS Microanalyzer). ZAF matrix correction factors were applied in instrumental software calculations.

Sintering behavior

The density of bulk glass-ceramic specimens as well as sintered specimens was measured by Archimedes' method. The degree of sintering was calculated assuming 100% theoretical density for bulk heat treated glass-ceramic specimens. The sintering behavior was also assessed by scanning electron microscopy on both as-sintered and sintered and polished specimens.

Statistical methods

Results were analyzed by ANOVA and Tukey's test to detect statistically significant differences. A *p*-value of less than 0.05 was considered statistically significant.

Results

Crystallization behavior

Characteristic X-ray powder diffraction patterns of specimens sintered at 775, 800 or 900°C for 1h are displayed in Figure 1 (A-D). Fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$, PDF 15-876) was present for all compositions from 775°C and up. The figure of merit for fluorapatite was determined using PDXL 2 Data Analysis Software on precision scans performed at 0.2 degree per minute (Figure 1D) and was less than one for all compositions, indicating an excellent match. Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$, PDF 35-592) started to appear at 775°C for composition D and 900°C for composition C. It became the predominant phase at 800°C for composition D. A small amount of forsterite (Mg_2SiO_4 , PDF 34-189) was found in composition D after heat treatment at 800°C and in all compositions at 900°C. X-ray powder diffraction patterns obtained on disks sectioned from bulk glass ingots and further heat treated matched those of sintered specimens. Results from differential thermal analyses are summarized in Table 2 and graphically displayed in Figure 2. For each glass composition, two exothermic peaks were observed. For all compositions, the first exotherm, occurring between 783 and 864°C, is attributed to the crystallization of fluorapatite. According to XRD analyses, the second exotherm, occurring between 981 and 1074°C, is attributed to the crystallization of forsterite in compositions A and B and concurrent crystallization of akermanite and forsterite in compositions C and D. The Optimum Nucleation Temperature varied between 670 and 700°C, depending on the composition. The plots obtained from the Kissinger equation (1) are shown in Figure 2. The activation energy for the crystallization of fluorapatite slightly increased with increasing the calcium to aluminum ratio and ranged between 343kJmol^{-1} for composition A to 353kJmol^{-1} for composition D.

The results from dilatometric analyses, including the softening point and coefficient of thermal expansion are listed in Table 2. Increasing the calcium to aluminum ratio led to a decrease of the softening point from 725°C for composition A to 663°C for composition D, while the coefficient of thermal expansion increased from 9.5 to $11.5 \times 10^{-6}/^\circ\text{C}$.

The microstructure of the glass-ceramics after heat treatment at 800°C is shown in Figure 4A-D. A fine coast-and-island relict microstructure, characteristic of glass-in-glass phase separation, followed by crystallization of island-shaped fluorapatite crystals can be seen in composition A. Spherulitic fluorapatite crystals are present in compositions B and C, while well developed, flower-shaped fluorapatite crystals are clearly seen in composition D. The evolution of the microstructure with heat treatment temperature for composition D is

displayed in Figure 5 (A-D). Darker island-shaped akermanite crystals started to appear at 800°C, became more defined at 850°C and dominated the microstructure at 900°C. Results from EDS analyses are summarized in Table 3.

Sintering behavior

Results for density measurements of bulk glasses and glass-ceramics are presented in Table 4. The calculated degree of sintering as a function of temperature is graphically displayed in Figure 6. The lack of mechanical integrity prevented accurate measurement for compositions A and B after sintering at 700°C for 1h. The degree of sintering for composition A only remained around 60%, even after sintering up to 1050°C for one hour. The degree of sintering for composition B increased slowly from 63.5% at 750°C up to a maximum of 74.4% at 950°C for 1h. Concurrently, significant changes in the degree of sintering were observed for compositions C and D over the same temperature range. The largest amount of sintering occurred between 700 and 775°C for both compositions. Composition C reached a maximum of 91% after sintering at 900°C, followed by a linear decrease to 75% as the sintering temperature was raised to 1050°C. The degree of sintering of composition D rapidly reached 99% at 775°C and remained in this range up to 950°C, while a slight decrease in density was observed to 93.7% at 1050°C. Above 700°C, the overall degree of sintering was significantly different between all compositions ($p < 0.0001$). Composition D exhibited the greatest degree of sintering followed by C, B and A. Within groups C and D, sintering at 1050°C led to a significantly lower degree of sintering than other temperatures ($p < 0.0001$).

Scanning electron micrographs of specimens sintered at 775°C for 1h are shown in Figure 7 (A-D). Sharp-angled particles, indicating a lack of sintering, were present for composition A (Figure 7A). Rounding of the powder particles occurred for composition B, together with some particle necking (Figure 7B), while interconnected pores remained. A noticeably greater degree of necking, with progressive disappearance of open pores is evident for composition C (Figure 7C). Only a few pores remain and individual particles are no longer discernable for composition D, indicating that the sintering process is complete (Figure 7D). The microstructure after sintering at 800°C for 1h for composition D is shown in Figure 8. Flower-shaped fluorapatite crystals similar in shape and size to those observed after heat treatment of bulk specimens at 800°C for 1h are present.

Discussion

XRD and DSC results revealed that increasing the calcium to aluminum ratio led to a significant increase from 783 to 864°C in the crystallization temperature of fluorapatite, accompanied by a slight increase in the activation energy from 343 to 353 kJmol⁻¹. Meanwhile, the softening temperature decreased from 725°C to 663°C. We previously reported that glasses in the compositional range corresponding to composition A underwent amorphous phase separation, with formation of a droplet phase that later crystallized into small spherical fluorapatite crystals [15, 16]. This particular glass composition has a measured Ca:P ratio of 1.8, with phosphorous being the limiting element to the amount of fluorapatite crystallization. The remaining glassy matrix after FAp crystallization is likely to contain a small amount of fluorine, but very little calcium. Concurrently, composition D has a measured Ca:P ratio of 4.1, phosphorous being again the limiting factor to FAp crystallization, the remaining glassy matrix will contain a substantial amount of calcium. This explains the crystallization of akermanite (Ca₂MgSi₂O₇), immediately following that of fluorapatite. The activation energy for fluorapatite crystallization falls within the range of 163 to 682 kJ mol⁻¹ reported for other FAp glass-ceramic systems [43]. The slight increase in activation energy for composition D in bulk form was not expected due to the increase in

the amount of calcium in the composition. Calcium is a network modifier, expected to lower glass network connectivity and increase viscous flow, thereby inducing a decrease in the activation energy for FAp crystallization. O'Flynn *et al.* used a similar experimental design for DSC analyses, with determination of the optimal nucleation temperature and a nucleation hold, to study the crystallization behavior of apatite-mullite glass-ceramics [18]. They first determined the optimal nucleation temperature, and then applied a one hour nucleation hold at that temperature prior to investigating the effect of heating rate on the crystallization exotherms temperature. They observed an increase in the activation energy for fluorapatite crystallization with increasing the amount of calcium fluoride in the glass, with values in the range 292 to 471 kJmol⁻¹. It was proposed that higher amounts of fluorine led to a higher nucleation density during the isothermal hold. The creation of these nuclei consuming fluorine could have made crystal growth more difficult, hence increasing the activation energy. The apatite nucleation rate is also likely to increase with increasing the amount of calcium in the glass [44]. We propose that a similar mechanism involving a higher nucleation rate and/or phase separation of a calcium-rich phase, in relation with the subsequent crystallization of akermanite be responsible for a slightly more difficult crystal growth in composition D, ultimately leading to an increase in the activation energy and crystallization temperature of fluorapatite. Although semi-quantitative, EDS analyses confirmed that glass melting was associated with significant fluorine losses by volatilization. They also showed losses in other species such as phosphorous and potassium. However, fluorine losses were anticipated and excess fluorine remained in all compositions with regard to the stoichiometry of fluorapatite, most certainly playing an important role on the behavior of the glasses, by lowering network connectivity and further promoting phase separation [45, 46]. As the glasses phase-separated into Ca-P-rich droplets [16], modifier cations were no longer needed to charge-balance phosphorous in the glass network, allowing a decrease in connectivity. Meanwhile, increasing the amount of charge-balancing calcium available and decreasing the amount of aluminum is likely to have prevented Al³⁺ ions from reaching a four-fold coordination state, also leading to a decrease in connectivity. Therefore, we hypothesize that both calcium and fluorine led to a decrease in network connectivity, permitting better sintering by viscous flow prior to fluorapatite full crystallization. The observed increase in FAp crystallization temperature, together with a decrease in softening temperature considerably extended the processing window for compositions C and D, which explains the large increase observed in the degree of sintering as a function of calcium to aluminum ratio. This result is also in line with the overall decrease in the glass transition temperature and increase in coefficient of thermal expansion, reported to occur with an increase in CaO/SiO₂ ratio in diopside-fluorapatite-wollastonite-based glass-ceramics [31].

Sintering started and nearly reached completion prior to crystallization of fluorapatite in compositions C and D. The poor sintering behavior observed for compositions A and B is likely due to earlier crystallization of fluorapatite, together with lower amounts of calcium in the glassy matrix, compared to compositions C and D, thereby hindering the sintering process by increasing the viscosity. The crystallization of forsterite (Mg₂SiO₄) at higher temperatures further prevented sintering.

Spherulitic crystallization of fluorapatite was observed in glass-ceramics B, C and D after heat treatment at 800°C. According to Granasy: “spatial heterogeneities due to phase separation can provide a source of static disorder giving rise to spherulitic growth” [47]. As mentioned earlier, glass-in-glass phase separation occurs in our compositional range. Moreover, this type of apatite growth was first reported by Carpenter *et al.*, in phase-separated calcium alumino-silicate glasses nucleated with P₂O₅ [48], and later described by Shyu and Wu in MgO-CaO-SiO₂-P₂O₅ glasses [49]. More recently, Stanton and Hill reported spherulitic heterogeneous nucleation in apatite-mullite glass-ceramics, with an interesting mechanism: phase separation first occurred into amorphous droplets rich in Ca, P

and F, surrounded by regions rich in Si and Al [50]. The ensuing crystallization of fluorapatite left the surrounding glass depleted in Ca, P and F, and close to the composition of mullite. As mullite crystallized, the surrounding glass in turn became enriched in Ca, P and F and fluorapatite formed again. A similar scheme could be happening in composition D, with fluorapatite spherulites crystallizing first, followed by akermanite. This could explain the interpenetrating microstructure obtained after heat treatment at 850°C, temperature at which both phases co-exist. As shown on Figure 4, it is also possible that the phase-separated area grew larger as the calcium to aluminum ratio increased from composition A to D, leading to progressively larger spherulites.

This work demonstrated that compositions C and D are excellent candidates for the production of bioactive ceramic scaffolds by sintering at temperatures as low as 775°C. The unique microstructure conveyed by spherulitic crystallization of fluorapatite may provide an excellent basis for epitaxial growth of apatite crystals. Further crystallization of akermanite could impart additional attractive properties such as enhanced stimulation of cell differentiation into osteoblastic lineage, as suggested by recent studies on sintered akermanite ceramics [51-54].

Conclusions

Increasing the calcium to aluminum ratio led to both a decrease in softening temperature and an increase in crystallization temperature and activation energy for fluorapatite in this compositional range. This led to a widening of the processing window and made possible sintering to near theoretical density at temperatures between 775 and 800°C for compositions C and D, corresponding to the highest amounts of calcium.

Fluorapatite crystallized following a spherulitic pattern, with increasingly larger spherulites as the calcium to aluminum ratio increased. This microstructure may provide excellent conditions for epitaxial apatite deposition *in vivo*, as it mimics carbonated apatite crystal habits. The crystallization of akermanite could lead to enhanced stimulation of cell differentiation.

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Figure 1.

X-ray diffraction patterns of the various glass-ceramics after heat treatment for one hour at 775°C (A); 800°C (B and D); 900°C (C). X-ray conditions for scans in Figure 1D: 40 kV, 44mA, 0.2 deg/min., Si powder calibration standard (NIST 640d).

Figure 2. Kissinger plots of $\ln(v/T_p^2)$ as a function of $1/T_p$ for each of the glass compositions.

Figure 3.
DSC traces of each glass composition in bulk form (heating rate: $20^{\circ}\text{C}.\text{min}^{-1}$).

Figure 4. Scanning electron micrographs of the various glass-ceramics after heat treatment at 775°C for 1 hour. Composition A: (A); Composition B (B); Composition C: (C); Composition D: (D).

Figure 5. Scanning electron micrographs of glass-ceramic D after heat treatment at 775°C (A); 800°C (B); 850°C (C); 900°C (D).

Figure 6.
Degree of sintering as a function of sintering temperature for the various glasses.

Figure 7. Scanning electron micrographs of the various glass-ceramics after sintering at 775°C for one hour. Composition A: (A); Composition B (B); Composition C: (C); Composition D: (D).

Figure 8.
Scanning electron micrograph of glass-ceramic D after sintering at 800°C for one hour.

Table 1

Chemical composition of the glasses prepared (mol.%).

Composition	A	B	C	D
SiO ₂	33.9	33.1	32.3	31.5
MgO	22.9	22.3	21.8	21.2
Nb ₂ O ₅	0.3	0.2	0.2	0.2
CaO	8.6	13.9	19.0	23.9
Na ₂ O	2.5	2.4	2.4	2.3
K ₂ O	4.1	4.0	3.9	3.8
Al ₂ O ₃	10.4	7.1	3.9	0.9
CaF ₂	12.0	11.8	11.5	11.2
P ₂ O ₅	5.4	5.2	5.1	5.0

Table 2

DSC and dilatometric analyses summary: glass transition (T_g), crystallization exotherms (T_p), optimum nucleation temperature (ONT), fluorapatite activation energy (E_a), coefficient of thermal expansion (α) and softening point (T_s) for the various glass compositions.

Glass code	A	B	C	D
Ca/Al at. ratio	1	2	4	19
T_g bulk ($^{\circ}\text{C}$)	659	663	660	638
T_{p1} onset ($^{\circ}\text{C}$)	765	809	823	817
T_{p1} bulk ($^{\circ}\text{C}$)	783	833	861	864
T_{p2} bulk ($^{\circ}\text{C}$)	1062	1074	1025	981
ONT ($^{\circ}\text{C}$)	670	700	690	680
E_a fluorapatite (kJmol^{-1})	343	344	348	353
T_s ($^{\circ}\text{C}$)	725	704	693	663
α ($\times 10^{-6}/^{\circ}\text{C}$)	9.5	10.0	11.1	11.5

Table 3

Chemical composition (at.%) from EDS analyses (SD).

Element	A	B	C	D
O	60.0 (2.7)	56.3 (2.7)	59.3 (3.5)	52.8 (4.6)
F	3.3 (0.6)	2.7 (1.3)	3.5 (0.9)	3.1 (1.1)
Na	2.9 (0.7)	2.1 (0.9)	2.3 (0.3)	1.8 (0.3)
Mg	7.1 (0.4)	7.5 (3.1)	7.2 (0.6)	7.9 (1.0)
Al	6.2 (0.5)	4.9 (2.0)	2.9 (0.3)	1.1 (0.2)
Si	11.6 (1.0)	13.1 (5.4)	12.2 (1.8)	14.9 (2.4)
P	2.5 (0.2)	2.8 (1.2)	2.7 (0.4)	3.3 (0.5)
K	1.7 (0.3)	1.5 (0.7)	1.1 (0.1)	1.1 (0.1)
Ca	4.4 (0.5)	8.8 (3.8)	8.7 (1.4)	13.6 (2.0)
Nb	0.3 (0.1)	0.3 (0.1)	0.3 (0.1)	0.4 (0.1)

Table 4

Density of glasses and glass-ceramics.

Composition	Glass	Glass-ceramic
A	2.769 ± 0.008	2.852 ± 0.008
B	2.842 ± 0.008	2.886 ± 0.008
C	2.895 ± 0.012	2.887 ± 0.014
D	2.927 ± 0.008	2.951 ± 0.005