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Lithium metasilicate glass-ceramic fabrication using spark plasma sintering

Mohammad Khodaei[1], Farahnaz Nejatidanesh[2], Omid Savabi[3], Lobat Tayebi[4]

[1]Materials Engineering Group, Golpayegan College of Engineering, Golpayegan, Isfahan University of Technology, [2]Dental Materials Research Center, Dental Research Institute, School of Dentistry, Isfahan University of Medical Sciences, [3]Dental Research Center, Dental Research Institute, School of Dentistry, Isfahan University of Medical Sciences, Isfahan, Iran, [4]Marquette University School of Dentistry, Milwaukee, WI, USA

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Address for correspondence:
Dr. Farahnaz Nejatidanesh, Dental Materials Research Center, Dental Research Institute, School of Dentistry, Isfahan University of Medical Sciences,Isfahan, Iran.
E-mail: nejati@dnt.mui.ac.ir

ABSTRACT

Background: The digital dentistry, requires materials with wo opposite properties of machining ability and also enough hardness. The main objective of this experimental study was to investigate the fabrication feasibility of the lithium metasilicate glass-ceramic in partially crystalized stated using the spark plasma sintering (SPS) method.

Materials and Methods: In this study, SPS for the first time was used to fabricate primary lithium metasilicate glass-ceramic (LMGC) blocks. The raw materials were mixed and melted and then quenched in water and the resulted frits were grinded. The resulting powder was sintered by SPS at 660, 680, and 700°C.

Results: Scanning Electron Microscope (SEM), X-ray diffraction (XRD), and Vicker's microhardness assay were used to evaluate the properties of samples. Statistical comparison of the obtained data was performed by ANOVA, followed by the *post hoc* test of Duncan. Microstructural studies by SEM and XRD showed that all samples were composed of lithium metasilicate phase in a glassy matrix. With increasing the sintering temperature, the number and size of lithium metasilicate particles increased and higher mechanical properties have been achieved. However, the sintered sample at 700°C has less processing ability than the samples sintered at 660 and 680°C.

Conclusion: The optimum sintering temperature for glass frit consolidation was determined by SPS at 680°C.

Key Words: Biocompatible materials, ceramics, crystallization

INTRODUCTION

Lithium disilicate glass ceramics (LDGCs) are good candidates for computer-aided design and computer-aided manufacturing (CAD/CAM) of dental restoration.[1] After machining, lithium metasilicate glass-ceramics are heat treated to transformed to lithium disilicate and their microstructural changes, increase their rigidity and hardness, making them virtually nonmachining and hard material.[1] LDGCs are promising candidates for dental restoration, because of their excellent mechanical, optical, and biological properties and appropriate esthetics,[1,2] and enough biocompatibility.[2-4] The commercial blocks of lithium metasilicate glass-ceramic (LMGC) are fabricated using melting technology.[2] Dentists receive

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this material in partially crystalized (PC) condition and use it for layered or monolithic anterior and posterior veneers, crowns, and three-unit fixed dental prostheses which experience heavy occlusal forces.[2] As received LMGCs (PC condition) are composed of lithium metasilicate (LMS: Li_2SiO_3) crystals in a glassy matrix,[5] which have machining ability and are strong enough for CAD/CAM machining and appropriate edge stability.[6] The microstructure of this kind of glass-ceramic affects its mechanical properties significantly,[7] and their microstructure is affected by two factors of heat treatment cycle[7,8] and chemical composition.[7,9] Ortiz *et al*.[6] characterized the microstructural properties of IPS e.max CAD before and after heat treatment, and stated that nonfired blue block of IPS e.max (as received block or PC condition) include about 40 Vol.% crystals (mainly: LMS) and small amount of Li_3PO_4 and $Li_2Si_2O_5$) in a glassy matrix. After machining to the desired shape, a heat treatment cycle performs on samples for phase transformation to lithium disilicate crystals (LDS: $Li_2Si_2O_5$) and enhance its mechanical properties.[10] Because of interlocked arrangement of lithium disilicate crystals in fully crystalized condition (FC state), the glass-ceramic will have higher mechanical properties and fewer machining abilities.[6]

Ye *et al*.[11] cold pressed and sintered (at 860°C), the parent glass was obtained from two different routes of sol–gel and melting methods. The obtained samples consisted of LDS and did not have appropriate machining ability.[11] Al Mansour *et al*.[12] also fabricated fully crystalized samples using spark plasma sintering (SPS), which cannot be machined to the desired shape, because of LDS formation, while the machining ability is one of the most important features of this material application in dentistry.

SPS is an advanced technique of powder metallurgy which uses electric current and pressure for the consolidation and compaction of materials. In comparison with conventional powder metallurgy methods, SPS can heat the sample rapidly because the heat is generated by the electrothermal effect and distributed only within the die-punch system rather than throughout the whole furnace chamber. SPS is a relatively new powder metallurgy method for the rapid fabrication of advanced materials, and this technique can endow materials with outstanding properties.[13]

To the best of our knowledge, fewer studies were performed for the fabrication of lithium metasilicate in the PC state, and in the most of research, the lithium disilicate was processed directly to the FC state.

In the case of chemical composition, some constituents are added to the parent glass to improve the properties of the final parts. For example, the P_2O_5 acts as a nucleating agent, and its increasing, shifts the crystallization temperatures toward higher values.[14] Furthermore, K_2O leads to a decrease in the crystal growth rate and results in smaller crystal size,[15] and Al_2O_3 enhances the chemical durability of the glass.[16]

In this research, the blocks of partially crystallized lithium metasilicate glass-ceramic were fabricated using high-pressure SPS for the first time. To avoid lithium disilicate formation (which have high hardness and have not machining ability), we have to try sintering at fewer temperatures. Hence, SPS at high pressure has been employed for the first time. The SPS method is used to consolidate the powders at fewer temperatures than conventional powder metallurgy routes or melting technology. Furthermore, while the powders are in compaction pressure during sintering, so fewer residual micro pores will form in the matrix.[12]

MATERIALS AND METHODS

Glass fabrication

In this experimental study, we have tried to fabricate LMGC in PC state to have machining ability,[16] so to inhibit possible LDS crystallization during SPS, higher value of P_2O_5 (2 mol.%) is selected to add to the multi-component parent glass.[9,14] Actually, powder compaction using melting technology or powder technology requires high temperatures. This high temperature will lead to fully crystallization of lithium silicate (which will not have machining ability). Hence, to reduce the processing temperature for powder compaction, for the first time, the high-pressure SPS method is used.

The glass including the molar composition of 65.0 SiO_2-27.5 Li_2O-2.0 P_2O_5-2.0 K_2O-2.0 Al_2O_3-1.5 ZrO_2 was fabricated by melting raw materials of SiO_2, Li_2CO_3, Al $(PO_3)_3$, K_2CO_3, Al_2O_3, and ZrO_2 (which all of them were purchased from Merck company) in a platinum crucible at 1450°C for 1 h. The molten glass was poured in distilled water for rapid cooling and glass frit formation.[5] The frit was dried, ground, and re-melted at 1450°C for 1 h to improve the homogeneity. The molten glass was poured in distilled

water for rapid cooling and glass frit formation. After grinding and sieving to a particle size of smaller than 43 μm, differential scanning calorimetry (DSC) was used to study the thermal behavior of the sample and determine appropriate heat treatment conditions for partially crystallization.

Glass-ceramic block fabrication

SPS technique was used for glass powder densification and partially crystallization. The frit powder was poured in a graphite mold (cylinder shape with diameter and height of 10 mm) and placed in SPS machine (Chakad Sanat Spadan, Iran) at an initial pressure of 20 MPa. Sintering of precompacts was performed by increasing the temperature at a heating rate of 100°C/min, up to 660, 680, and 700°C under vacuum conditions (1.33 Pa), while the final temperature and final pressure of 200 MPa were applied for 5 min. While the thermal shock can affect the mechanical properties of the samples, so, the cooling rate was set on 3°C/min to room temperature to prevent thermal shock.[17] The final pressure was much greater than the usual values of conventional SPS processing, to insure complete compaction of frits.[18] The final temperatures of the sintering (660, 680, and 700°C) were chosen to be higher than the glassy temperature (Tg) and lower than the crystal phase transformation (LMS to LDS transformation) temperature.

Sample characterization

Differential scanning calorimetry

A calorimeter (Netzsch DSC 404F1 Pegasus) was used to study the thermal properties of the glass frit. The sample was heated from room temperature to 1000°C with a heating rate of 5°C/min to study the thermal behavior and detect any phase transformation phenomenon of lithium disilicate glass.

Phases analysis

X-ray diffraction (XRD: Philips X'Pert-MPD, Netherlands) was measured to identify the phases present in the glass frit and the sintered samples. X-rays were generated using the Cu-Kα lamp with the wavelength of 1.54060 A° in the range of 20°–80°. Quantitative analyses (Rietveld method) were used to determine the weight percent of phases (crystallinity) and also the Delf model of Rietveld was used to calculate the crystallite size of the crystalline phase using MAUD software.

Microstructural study

After polishing one surface of sintered samples using SiC abrasive paper to grit number of 2500, samples were etched using HF 3 wt.% solution (to dissolve the glassy matrix[4]), and then, a scanning electron microscope (SEM: Philips XL-30, Netherlands) was used in backscattered electron modes to investigate the microstructure of sintered samples. The number and size of the crystals were analyzed using the ImageJ software.

Mechanical properties

The indentation test was performed using a Vicker's hardness tester (FM-700, Future-Tech Corp, Kanagawa, Japan) using a square-based pyramidal shape with a tip angle of 136° diamond indenter and a load of 1 kg and 10 s dwell time, in accordance with the ASTM E384-17 standard, to calculate the hardness and fracture toughness of samples (Equations 1 and 2). Each test was repeated five times and the average values were reported.

$$Hv = 0.1891F/d^2 \quad (1)$$

$$K_{1C} = 0.016 \times (E/Hv)\ 0.5 \times (F/C1.5) \quad (2)$$

where, Hv is the Vickers hardness, F the applied load (N), d the half-diagonal length left by the indenter (mm), K_{1C} the fracture toughness (MPa. m1/2), E the modulus of elasticity (GPa), and C the mean half-length of the radial cracks from the impression center (mm).[17]

Statistical analysis

Statistical comparison of the obtained data was performed by ANOVA, followed by the *post hoc* test of Duncan. For the performed tests, the number of repetitions was considered three, and the results were reported as the mean ± standard deviation (SD).

RESULTS

The quenched frits were transparent, like glass. It is evident that the samples are glassy (noncrystalline). However, after sintering, they became opaque, may be because of crystalline phase formation [Figure 1], which will be investigated using XRD analysis. Furthermore, high-pressure SPS sintering of the samples at 660 and 680°C was performed easily and without any difficulty and problem, but, sometimes, high-pressure SPS sintering of the samples at 700°C accompanied by mold fracture, it seems, sintering at 700°C had fewer processing ability than two other temperatures.

Thermal analysis

Figure 2 shows the DSC curve of the parent frit from ~300°C to 1000°C in an air atmosphere. The

glass transition temperature (Tg) and two exothermic peaks (T_1 and T_2) attributable to Li_2SiO_3 and $Li_2Si_2O_5$ formation, and melting temperature (T_m) of frits are at 402, 694, 851, and 970°C, respectively.

Base on the result of DSC and previous literature,[5,12] three different temperatures of 660, 680, and 700°C were selected for the densification of samples using SPS. According to the results of DSC analysis, the temperature of Li_2SiO_3 and $Li_2Si_2O_5$ formation is 694 and 851°C, respectively. While the main purpose of this study is to fabricate LMGC, so the selected temperatures must be smaller than the temperature of $Li_2Si_2O_5$ formation (851°C, respectively), so the temperatures of 660, 680, and 700°C were selected for the densification of samples using SPS.

Phases analysis

The XRD pattern of the frit (quenched molten glass in water) and sintered samples at 660, 680, and 700°C are presented in Figure 3. The diffraction pattern of the frit only consisted of the broad peak at the position of 20°–30°, indicating an amorphous structure of frit. While the XRD patterns of sintered samples include some sharp peaks related to a crystalline phase (LMS phase) and a broad peak related to a glassy matrix.

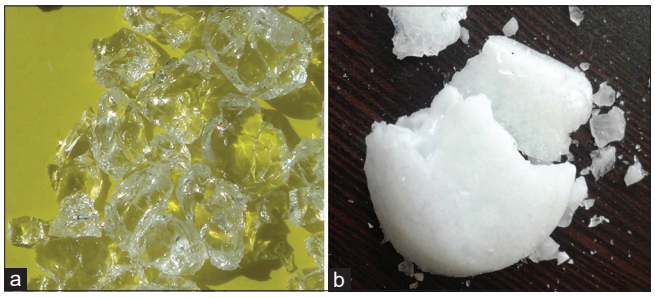

Figure 1: The images of (a) glassy frit, (b) partially crystallized sample using SPS at 680 C.

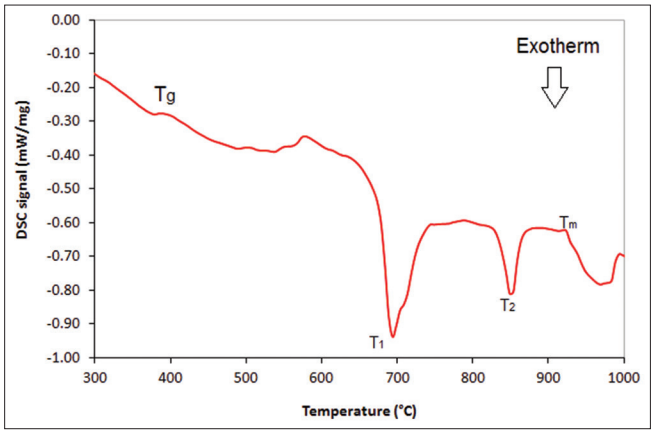

Figure 2: DSC curve of the quenched frit. DSC: Differential scanning calorimetry.

SEM observation

Figure 4 shows the SEM micrograph of sintered samples at 660, 680, and 700°C. All samples present a two-phase glass-ceramic structure, with ceramic crystals embedded in a glassy matrix.

Mechanical properties

The Vickers hardness of sintered samples at 660, 680, and 700°C were measured; and the mean values and SDs are 645 ± 8, 684 ± 7, and 691 ± 10, respectively. Furthermore, the fracture toughness of sintered samples at 660, 680, and 700°C are calculated (using equation 2) to be 2.23 ± 0.12, 2.45 ± 0.13, and 2.97 ± 0.15, respectively.

DISCUSSION

Bai *et al.*[5] reported the temperature values of 448, 588, 814, and 967°C for glass transition, Li_2SiO_3 and $Li_2Si_2O_5$ formation, and melting temperature, respectively. Moreover, Al Mansour *et al.*[12] reported these values 450, 620, 812, and 955°C for the commercial type of lithium disilicate before crystallization (the IPS e.max press). The differences can be because of different heating and cooling rates and the chemical composition of frits. It is evident that to fabricate PC glass ceramic, the frits must be heated under the temperature of $Li_2Si_2O_5$ formation. Sintering the frits at temperatures over the temperature of $Li_2Si_2O_5$ formation will result in Li_2SiO_3 to $Li_2Si_2O_5$ transformation and thus the obtained block will not have appropriate machining ability.

It seems quenching the molten glass in water, inhibited any crystallization during cooling, and the resulted a glassy frit formation. It is evident that the cooling rate was so high enough, to inhibit Li_2SiO_3 and $Li_2Si_2O_5$ nucleation and growth during quenching the molten glass from 1450°C into the water.

The diffraction patterns of all sintered samples using SPS at 660, 680, and 700°C included the presence of peaks related to lithium metasilicate (Li_2SiO_3: PDF No.: 01-072-1140) and there were no extra detectable phases. However, the height of sharp peaks of lithium metasilicate related to the broad and wide peak (2 θ = 20°–30°) is increased by increasing the sintering temperature. Actually, by increasing the sintering temperature, more portion of the glassy matrix is transformed to the crystalline lithium metasilicate phase. The height of sharp peaks of lithium

metasilicate was increased by increasing the sintering temperature, and also, their wideness was decreased by increasing the sintering temperature. This phenomenon can be because of increasing the crystalline size of lithium metasilicate particles at the glassy matrix. The quantitative assessment of XRD graphs using the Rietveld method shows that the glassy matrix of sintered samples at 660, 680, and 700°C was 46, 62, and 63 wt.%, respectively. It seems that with increasing the sintering temperature, more portion of the glassy matrix is transformed to crystalline phase.

Ortiz *et al.*[6] reported that the PC commercially available LDGC (IPS e.max CAD high translucency, C14, Shade A2; Ivoclar Vivadent, NY) consists of a glassy matrix and mainly LMS crystals (40 Vol.%), which this structure provides appropriate machining ability.

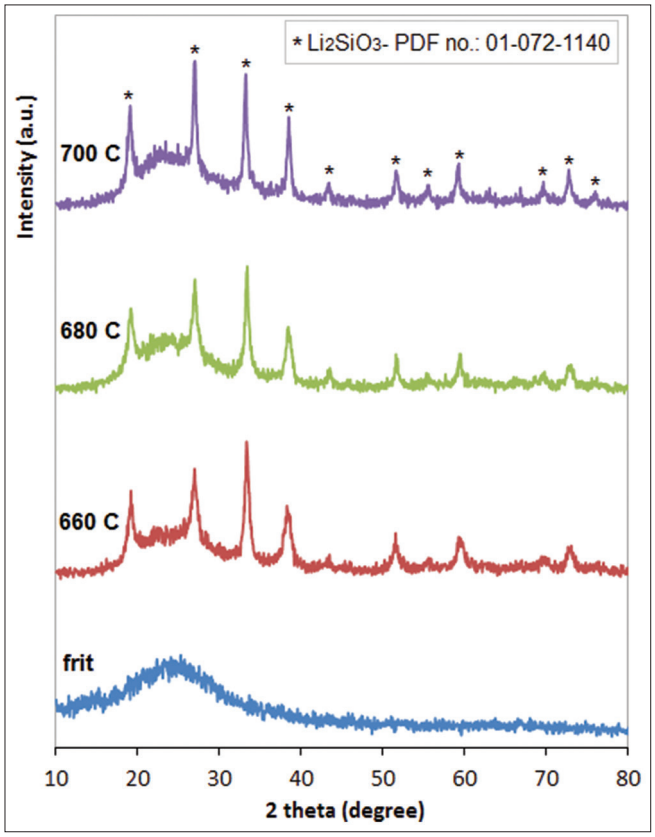

Figure 3: XRD patterns for lithium silicate frit and sintered samples at 660, 680, and 700°C. XRD: X-ray diffraction.

The size of rod-like crystals was almost the same for all samples. The length of rod-like crystals was about 3–5 μm in all samples. However, it is evident that the volume percent of porosity decreased by increasing the sintering temperature. The image processing of this figure using ImageJ software indicates that the volume percent of porosity is about 0.7 ± 0.1, 1.2 ± 0.2, and 1.6% ± 0.3% for sintered samples at 700, 680, and 660°C, respectively. It is evident that more powder densification happened, by increasing the sintering temperature. Furthermore, it is evident that LMS crystals are distributed randomly at the glassy matrix in all samples.

While the mechanical properties of ceramic dental materials are important for the clinical success of clinical restorations,[19] so investigating their mechanical properties is curial. The surface hardness of PC commercially available lithium disilicate blocks (IPS e.max CAD, Ivoclar Vivadent) sample was reported about 732 Hv, while it decreased to 696 Hv after one cycle of firing.[20]

According to Figure 5, the Vickers hardness of sintered samples at 660, 680, and 700°C are 645 ± 8, 684 ± 7, and 691 ± 10, respectively. It is evident that by increasing the sintering temperature, the hardness of samples is increased significantly. This phenomenon is because of increasing the LMS portion and size at the glassy matrix. Actually, the LMS particle act as reinforcement for glassy matrix. As reported in the result section, the fracture toughness of sintered samples at 660, 680, and 700°C are 2.23 ± 0.12, 2.45 ± 0.13, and 2.97 ± 0.15 MPa.m$^{0.5}$, respectively.

Meng *et al.*[20] heat treated the PC commercially available lithium disilicate blocks (IPS e.max CAD,

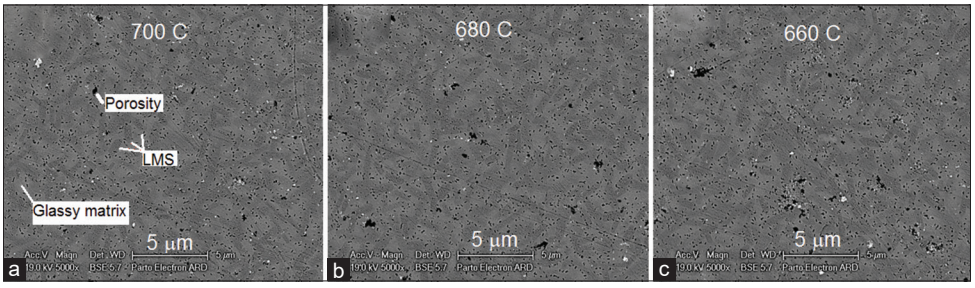

Figure 4: SEM micrographs for sintered samples at (a) 700°C, (b) 680°C, and (c) 660°C.

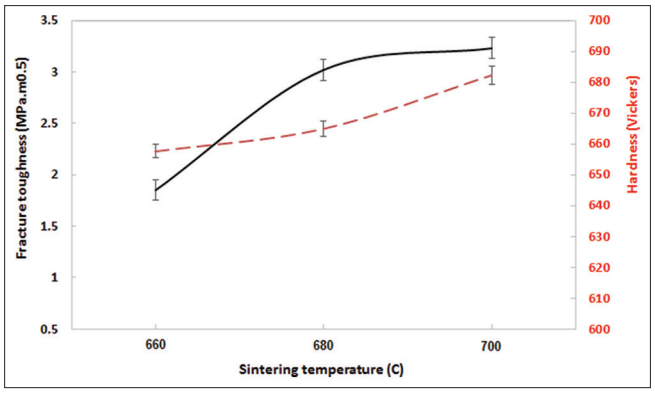

Figure 5: The hardness and fracture toughness of sintered samples at 700°C, 680°C and 660°C.

Ivoclar Vivadent) by multiple firing cycles and observed that the fracture toughness of samples increases by the first firing cycle (crystallization), and subsequent firing cycles will result in fracture toughness decrement, because of microstructural changes.

It is evident that by increasing the sintering temperature, the hardness of samples is increased significantly. This phenomenon can be because of porosity decrement at the glassy matrix and also better densification and powder particle bonding during sintering.

CONCLUSION

Partially crystallized lithium disilicate blocks are fabricated using SPS at higher compaction pressures than the powder metallurgy technique. The fabricated blocks had enough mechanical properties for handling and machining. The microstructure and mechanical properties of partially crystallized lithium disilicate blocks can be tailored by changing the sintering temperature. The fabricated partially crystallized lithium disilicate blocks are promising candidates for dental restoration fabrication using CAD/CAM.

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Conflicts of interest

The authors of this manuscript declare that they have no conflicts of interest, real or perceived, financial or nonfinancial in this article.

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