US009241879B2

(12) **United States Patent**
Castillo

(10) **Patent No.: US 9,241,879 B2**
(45) **Date of Patent: *Jan. 26, 2016**

(54) **LITHIUM SILICATE GLASS CERAMIC FOR FABRICATION OF DENTAL APPLIANCES**

(75) Inventor: **Rodolfo Castillo**, Boca Raton, FL (US)

(73) Assignee: **James R. Glidewell Dental Ceramics, Inc.**, Newport Beach, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 320 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **13/374,040**

(22) Filed: **Dec. 8, 2011**

(65) **Prior Publication Data**

US 2012/0094822 A1 Apr. 19, 2012

Related U.S. Application Data

(63) Continuation-in-part of application No. 12/592,825, filed on Dec. 3, 2009, now abandoned, which is a continuation-in-part of application No. 12/283,472, filed on Sep. 12, 2008, now Pat. No. 7,892,995, which is a continuation-in-part of application No. 12/082,576, filed on Apr. 11, 2008, now abandoned.

(51) **Int. Cl.**

C03C 10/04	(2006.01)
A61C 5/10	(2006.01)
A61K 6/027	(2006.01)
A61K 6/00	(2006.01)
A61K 6/02	(2006.01)
A61L 27/10	(2006.01)
C03C 3/097	(2006.01)
C03C 4/00	(2006.01)
C03C 10/00	(2006.01)

(52) **U.S. Cl.**

CPC ***A61K 6/0273*** (2013.01); ***A61K 6/0094*** (2013.01); ***A61K 6/021*** (2013.01); ***A61K 6/023*** (2013.01); ***A61K 6/024*** (2013.01); ***A61K 6/0215*** (2013.01); ***A61K 6/0245*** (2013.01); ***A61L 27/105*** (2013.01); ***C03C 3/097*** (2013.01); ***C03C 4/0021*** (2013.01); ***C03C 10/0027*** (2013.01)

(58) **Field of Classification Search**

CPC . A61K 6/0205; A61K 6/0215; A61K 6/0273; A61L 27/10; C03C 10/00; C03C 10/0009; C03C 4/0007

USPC 501/5, 7; 106/35

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,006,775	A	10/1961	Chen
4,189,325	A	2/1980	Barrett et al.
4,205,982	A	6/1980	German
4,480,044	A	10/1984	McAlinn
4,515,634	A	5/1985	Wu et al.
4,992,297	A	2/1991	Van der Zel
5,219,799	A	6/1993	Beall et al.
5,290,371	A	3/1994	Cameron et al.
5,698,019	A	12/1997	Frank et al.
5,744,208	A	4/1998	Beall et al.
5,968,856	A	10/1999	Schweiger et al.
6,342,458	B1	1/2002	Schweiger et al.
6,455,451	B1	9/2002	Brodkin et al.
6,514,893	B1	2/2003	Schweiger et al.
6,517,623	B1	2/2003	Brodkin et al.
6,606,884	B2	8/2003	Schweiger et al.
6,802,894	B2	10/2004	Brodkin et al.
6,818,573	B2	11/2004	Petticrew
7,316,740	B2	1/2008	Schweiger et al.
7,381,258	B2	6/2008	Krumbholz
7,452,836	B2	11/2008	Apel et al.
7,816,291	B2	10/2010	Schweiger et al.
7,867,930	B2	1/2011	Apel et al.
7,867,931	B2	1/2011	Apel et al.
7,871,948	B2	1/2011	Apel et al.
7,892,995	B2	2/2011	Castillo
8,042,358	B2	10/2011	Schweiger et al.
8,047,021	B2	11/2011	Schweiger et al.
2002/0198093	A1	12/2002	Van der Zel
2004/0197738	A1	10/2004	Ban et al.
2005/0155518	A1	7/2005	Krumbholz
2005/0288165	A1	12/2005	Krumbholz
2006/0194895	A1	8/2006	Loveridge et al.
2009/0256274	A1 *	10/2009	Castillo 264/16
2009/0258778	A1	10/2009	Castillo
2009/0291820	A1	11/2009	Schweiger et al.

(Continued)

FOREIGN PATENT DOCUMENTS

EP	2664594 A1	11/2013
WO	WO 2011/076422	6/2011
WO	WO 2012/059143	5/2012

OTHER PUBLICATIONS

Marcus P. Borom et al, Strength and Microstructure in Lithium Disilicate Glass-Ceramics, J. Am. Ceram. Soc., Sep.-Oct. 1975, vol. 58, No. 9-10, pp. 385-391.

R.A. Eppler, Glass Formation and Recrystallization in the Lithium Metasilicate Region of the System Li2O—A12O3—SiO2, J. Am. Ceram. Soc., Feb. 1963, vol. 46, No. 2, pp. 97-101.

(Continued)

Primary Examiner — Karl Group

(57) **ABSTRACT**

The present invention relates to a method of fabricating an improved lithium silicate glass ceramic and to that material for the manufacture of blocks for dental appliances using a CAD/CAM process and hot pressing system. The lithium silicate material has a chemical composition that is different from those reported in the prior art with 1 to 10% of germanium dioxide in final composition. The softening points are close to the crystallization final temperature of 800° C. indicating that the samples will support the temperature process without shape deformation.

7 Claims, 4 Drawing Sheets

(56) **References Cited**

U.S. PATENT DOCUMENTS

2010/0083706	A1	4/2010	Castillo
2011/0009254	A1	1/2011	Schweiger et al.
2011/0256409	A1	10/2011	Ritzberger et al.
2012/0148988	A1	6/2012	Castillo et al.

OTHER PUBLICATIONS

F.A. Hummel, Thermal Expansion Properties of Some Synthetic Lithia Minerals, J. Am. Ceram. Soc., Aug. 1951, vol. 34, No. 8, pp. 235-239.

Landolt-Börnstein (LB), Group IV Physical Chemistry—Phase Equilibria, Crystallographic and Thermodynamic Data for Intermediate Compounds in the Li2O—SiO2 System.

S. Claus et al, Phase Equilibria in the Li4SiO4—Li2SiO3 Region of the Pseudobinary Li2O—SiO2, Journal of Nuclear Materials, vol. 230, Issue 1, May 1996, pp. 8-11.

Herman F. Shermer, Thermal Expansion of Binary Alkali Silicate Glasses, Journal of Research of the National Bureau of Standards, vol. 57, No. 2, Aug. 1956.

PCT International Search Report in PCT/US2013/024692 dated Apr. 15, 2013.

* cited by examiner

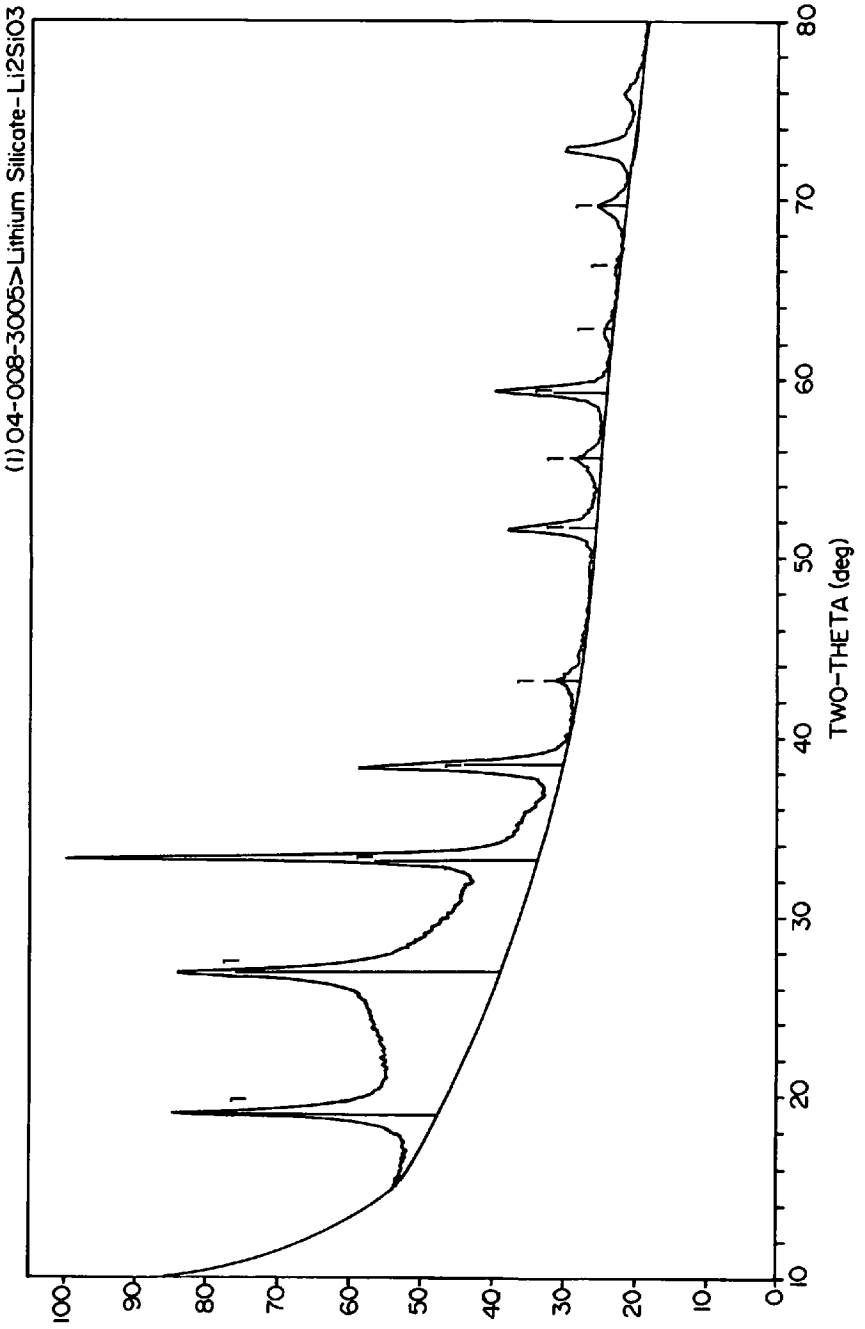
(1) 04-008-3005>Lithium Silicate-Li2Si03
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
TWO-THETA (deg)

FIG. 1

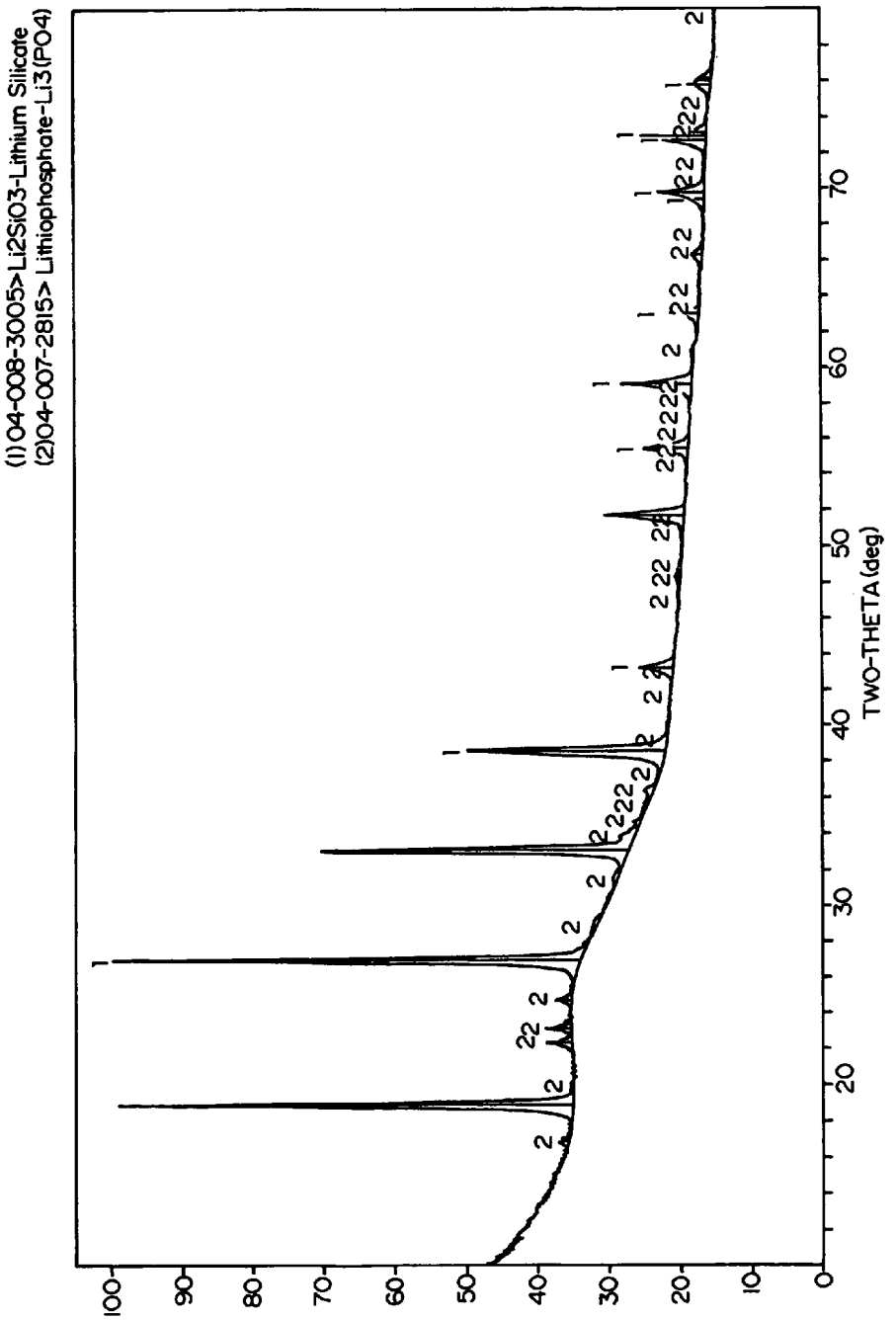
(1) 04-008-3005> Li2SiO3-Lithium Silicate
(2) 04-007-2815> Lithiophosphate-Li3(PO4)
TWO-THETA (deg)

FIG. 2

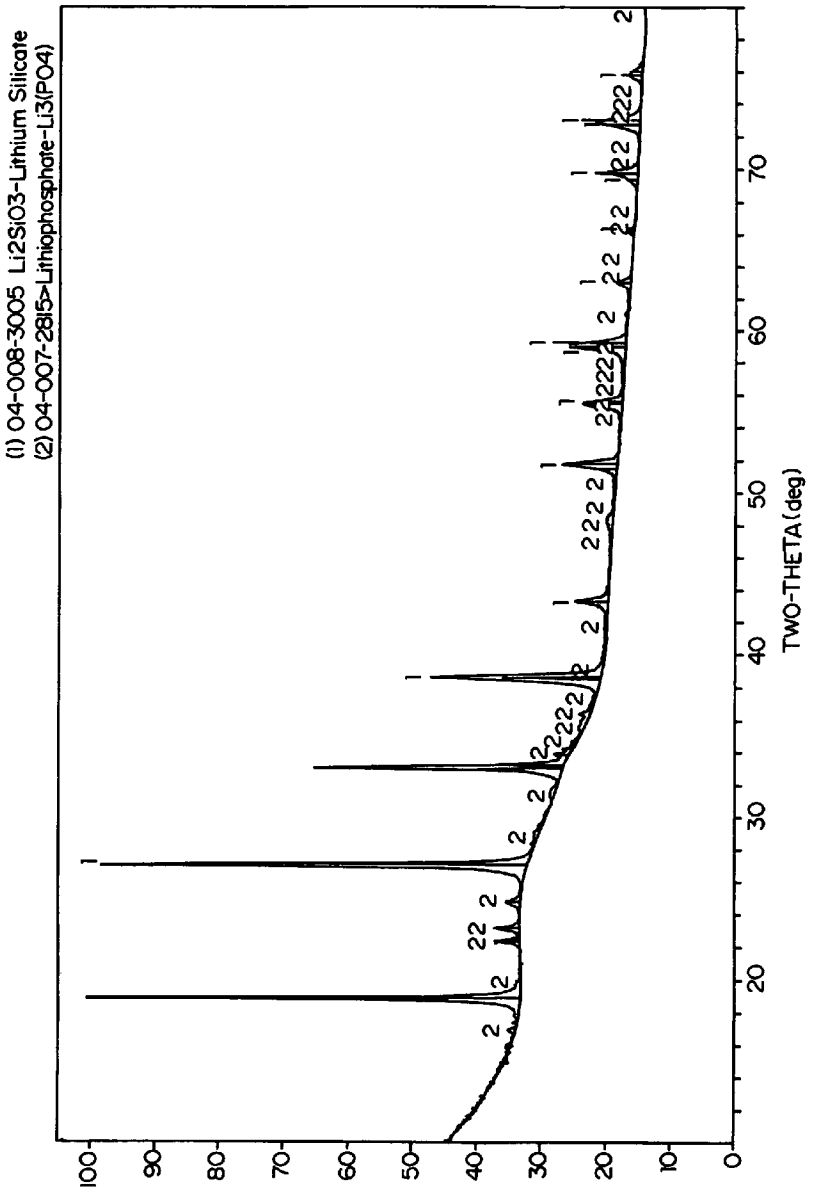
(1) 04-008-3005 Li2Si03-Lithium Silicate
(2) 04-007-2815>Lithiophosphate-Li3(PO4)
TWO-THETA (deg)

FIG. 3

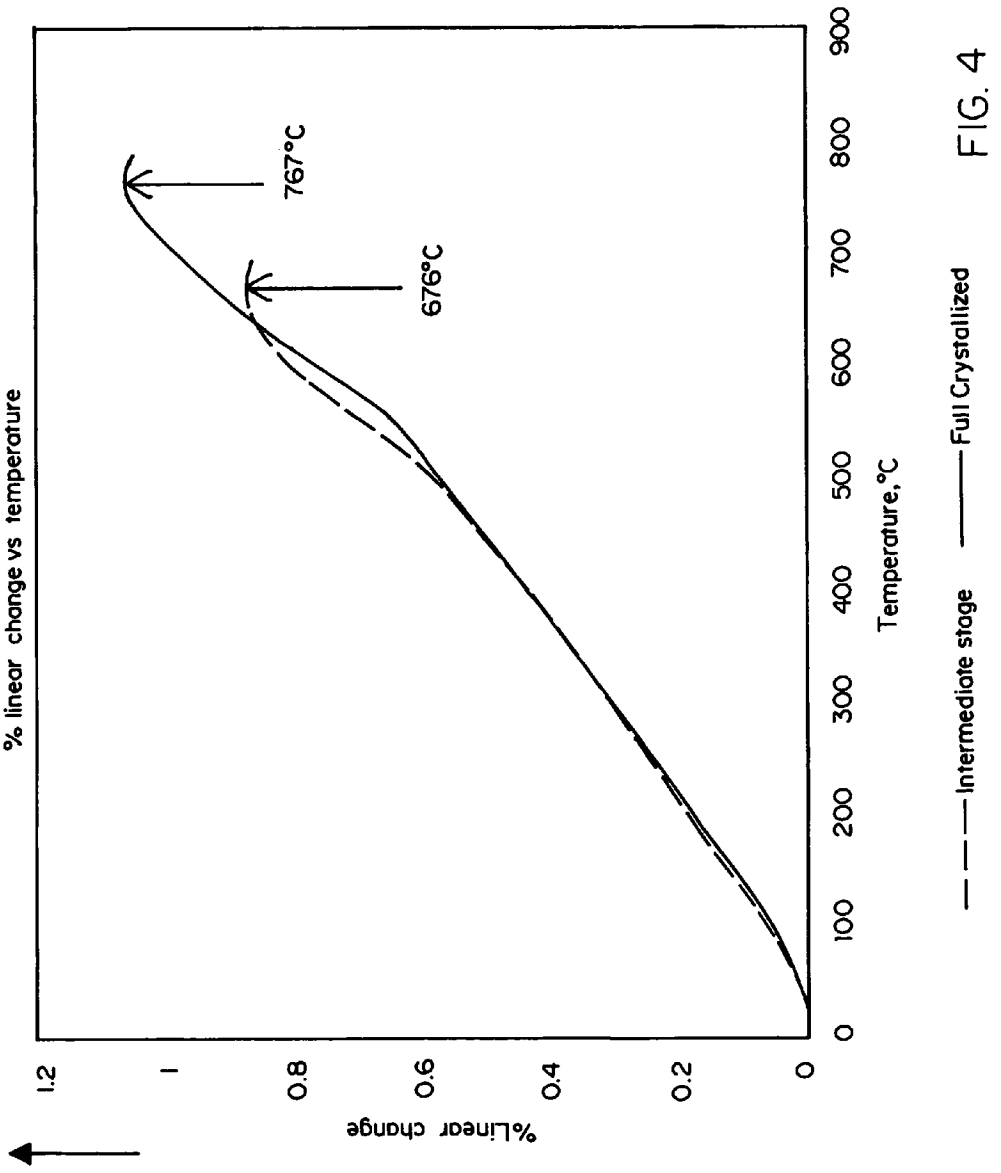
% linear change vs temperature
%Linear change
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
800
900
Temperature, °C
767°C
676°C
Intermediate stage
Full Crystallized

FIG. 4

LITHIUM SILICATE GLASS CERAMIC FOR FABRICATION OF DENTAL APPLIANCES

RELATION TO CORRESPONDING APPLICATIONS

This application is a continuation-in-part of U.S. patent application Ser. No. 12/592,825 filed Dec. 3, 2009, now abandoned, which, in turn, is a continuation-in-part of application Ser. No. 12/283,472 filed Sep. 12, 2008, now issued as U.S. Pat. No. 7,892,995, which, in turn, is a continuation-in-part of application Ser. No. 12/082,576 filed Apr. 11, 2008, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a lithium silicate glass ceramic material and a process for fabricating that material for the manufacture of blocks and subsequent fabrication of single crowns with the aid of a CAD/CAM process and hot pressing. The invention relates to an improved version of such glass ceramic containing germanium dioxide to make it more castable, with higher density, and with higher flexural strength than the lithium disilicate glass ceramic free of germanium dioxide.

2. Background Art

There are many products available that employ lithium disilicate glass ceramic covered by several U.S. patents. Some of these patents claim a process for the preparation of shaped translucent lithium disilicate glass ceramic products from a mixture of basic components (SiO_2, Al_2O_3, K_2O, Li_2O, plus pigments and fluorescent oxides). The thermodynamic solid-liquid equilibrium of the system consisting of lithium oxide (Li_2O) and silicon dioxide (SiO_2) has been extensively studied even before that material was used as a dental ceramic (1-3, 5-6).

For those skilled in the art this experimental solid-liquid equilibrium can explain with an extraordinary simplicity how different glass ceramics can be obtained using the same two components when they are combined in different proportions. The same solid-liquid equilibrium shows what type of stable crystal is produced as a final product of crystallization when a specific mix composition of the two components are blended, melted, and crystallized to achieve the final product.

The crystallographic data for intermediate crystal compounds in the Li_2O—SiO_2 system is given by the Landolt-Bomtein tables. The following are the types of crystal compositions possible in the Li_2O—SiO_2 system: Li_8SiO_6, Li_4SiO_4 or lithium orthosilicate monoclinic and orthorhombic; $Li_6Si_2O_7$, Li_2SiO_3 or lithium silicate; $Li_2Si_2O_5$ or lithium disilicate monoclinic and orthorhombic; and $Li_2Si_3O_7$ lithium trisilicate.

Thus when the silicon dioxide to lithium oxide molar ratio (SiO_2/Li_2O) is greater than or equal to two, meaning two moles of SiO_2 are mixed with one mol of Li_2O, the crystallized glass ceramic product will be mainly lithium disilicate (SiO_2/Li_2O). This molar ratio of two is equivalent to a molar composition of lithium oxide in the mixture of 33% (67% as SIO_2). When the same molar relationship is below 2.0, (e.g. 1.7) only lithium silicate crystals are produced ($Li_2O.SiO_2$). The lithium oxide molar composition for a ratio of 1.7 is equivalent to 37% molar (63% SiO_2). The type of resulting crystal due to the specific composition ratios gives to the glass ceramic its own distinguishable chemical and physical properties. Surprisingly, the same behavior is obtained if these two main components (silicon dioxide and lithium oxide) maintain their molar ratio below two even if they are mixed with other oxides as additives and modifiers. The other common oxides mixed are aluminum oxide, potassium oxide, calcium oxide, zirconium oxide and coloring oxides that are incorporated into the glass matrix and give the glass ceramic its final color and translucency.

Due to the final composition of this invention using a molar ratio of SiO_2/Li_2O between 1.7 to 1.9, the only phase present is lithium silicate, instead of lithium disilicate, as a main constituent of the glass ceramic as a final product. For instance, a glass ceramic with a molar ratio of silicon dioxide to lithium oxide greater than or equal to two plus additional oxides will produce, after full crystallization a lithium disilicate glass ceramic with a melting temperature of 920° C. and a linear thermal coefficient of expansion of 10.5×10^{-6}/° C. as a final product and composition. In addition, during the production of this type of glass ceramic the cast material is subjected to at least three different heat treatments: an annealing cycle for eliminating accumulated stresses, a nucleation cycle for the formation of lithium metasilicate or unstable lithium silicate, and finally a third thermal cycle to convert the unstable lithium silicate or metasilicate into a stable lithium disilicate. This is clearly shown in the following US patents:

Examples of those types of glass ceramics are claimed in Barret et al in U.S. Pat. No. 4,189,325 which discloses a lithium silicate glass ceramic where the raw materials are blended, melted at 1315° C. and held for 24 hours for homogenization, fritted and crushed, melted again and cast into preheated molds. They disclose a composition of silicon dioxide to lithium oxide molar ratio of two, producing a dental ceramic composed of lithium disilicate.

U.S. Pat. No. 4,480,044 to McAlinn discloses a glass ceramic formulation where the lithium silicate glass ceramic in their intermediate process stage has a thermal expansion of 13×10^{-6}/° C. and the lithium disilicate has a thermal expansion of 11.4×10^{-6}/° C. They disclose a machinable lithium disilicate glass ceramic with a percentage of silicon dioxide of 79.8%.

U.S. Pat. No. 4,515,634 to Wu et al discloses a castable glass ceramic composition useful as a dental restorative material. The components are blended and melted at 1400 to 1450° C., then quenched in water, dried, milled to a powder, and melted again at 1400° C. for 4 hours. Then the melt is cast into copper molds and transferred to the annealing process. The castable glass ceramic of the invention is lithium disilicate with a silicon dioxide to lithium oxide molar ratio of two, equivalent to silicon dioxide weight composition of 65%-74.7% and lithium oxide weight composition of 14.8-16.4%.

U.S. Pat. No. 5,219,799 to Beall et al discloses a lithium disilicate glass ceramic with silicon dioxide weight composition of 65%-80% and lithium oxide compositions of 8.0-19.0%. The blended raw materials are melted at 1450° C. for 16 hours and then poured into steel molds and annealed at 450° C.

U.S. Pat. No. 5,744,208 to Beall et al describes a lithium disilicate glass ceramic with silicon dioxide weight composition of 75%-95% and lithium oxide weight composition 3-15%. The raw materials are blended, and then melted in the range of 1450-1600° C. for about 6-10 hours. The glass is then poured into steel molds. The glass is then annealed, nucleated and crystallized to produce lithium disilicate glass ceramic in the range of 500° C. to 850° C.

U.S. Pat. No. 5,968,856 to Scheweiger et al discloses a lithium disilicate glass ceramic with compositions of silicon dioxide weight between 57%-80% and lithium oxide composition 11-19%. The components are blended and melted at 1500° C. for one hour and then quenched, dried, milled, dry

pressed and sintered to form blanks. The composition requires the addition of lanthanum oxide to improve the flow properties, control the crystal growth and eliminate the strong reaction of the material with the investment material used.

U.S. Pat. No. 6,514,893 to Scheweiger et al discloses a lithium disilicate glass ceramic with silicon dioxide composition of 57%-75% weight and lithium oxide composition 13-19% weight and also containing lanthanum oxide. The components are blended and fused into granulates and comminuted to a powder. Coloring oxides are then added, and the ceramic is pressed and heat treated.

U.S. Pat. No. 6,455,451 to Brodkin et al discloses a lithium disilicate glass ceramic with silicon dioxide composition of 62%-85% weight and lithium oxide composition 8-19% weight. They disclose a method of making the lithium disilicate by melting the components at 1200 to 1600° C., followed by a quench, drying, and a heat treatment to form the glass ceramic, followed by comminuting to a powder, compacting and sintering to a blank and pressing to form the restoration.

U.S. Pat. No. 6,517,623 to Brodkin et al discloses a lithium disilicate glass ceramic pressable where the components are melted in the range of 1200 to 1600° C., quenched, heat treated, comminuting the glass ceramic to a powder, and then compacting the powder to a starting blank before sintering the blank or the restoration.

U.S. Pat. No. 6,606,884 to Scheweiger et al describes a lithium disilicate glass ceramic where the components are mixed and melted at 1200 to 1650° C., followed by pouring the glass into water, milling and compacting, and placing the blank in a heat treatment to sinter.

U.S. Pat. No. 6,802,894 to Brodkin et al shows a lithium disilicate glass ceramic with a silicon dioxide weight composition of 62%-85% and lithium oxide weight composition 8-19%. The components are mixed, melted at 1200 to 1600° C., and cast. The resulting glass is annealed at a range of 300 to 600° C., followed by subjecting the glass to a heat treatment from 400 to 1100° C.

U.S. Pat. No. 6,818,573 to Petticrew discloses a lithium disilicate glass ceramic with a silicon dioxide composition of 60%-80% weight and lithium oxide composition of 8-17% weight. The components are blended, melted, quenched, heat treated, milled to a powder, dry pressed, and hot pressed into the desired restoration.

U.S. Pat. No. 7,316,740 to Scheweiger et al claims a lithium silicate glass ceramic with silicon dioxide weight compositons of 64 to 73% and lithium oxide weight compositions of 13 to 17%. The lithium disilicate final product is demonstrated by means of a XRD pattern (FIG. **6**) and DSC phase transformation curve from lithium metasilicate to lithium disilicate (FIG. **2**). The DSC diagram shows the change in energy from the stage of metasilicate to disilicate, which is only necessary if lithium disilicate is desired to be the crystal phase used as a final product.

U.S. Pat. No. 7,452,836 to Apel et al discloses a lithium silicate glass ceramic with silicon dioxide composition of 64%-75% weight and lithium oxide composition of 13-17% weight producing lithium disilicate as a final product. They also describe a glass ceramic with a molar ratio of silicon dioxide to lithium oxide of at least 2.3.

U.S. Pat. No. 7,867,930 to Apel et al shows a lithium silicate glass ceramic with silicon dioxide composition of 64%-75% weight and lithium oxide composition of 13-17% weight producing lithium disilicate as a final product.

U.S. Pat. No. 7,871,948 to Apel et al describes a lithium silicate glass ceramic with silicon dioxide composition of 64%-75% weight and lithium oxide composition of 13-17% weight, producing lithium disilicate as a final product. The glass of the starting material is subjected to an initial heat treatment form lithium metasilicate or unstable lithium silicate and then goes through a second heat treatment to convert the lithium metasilicate to a lithium disilicate.

U.S. Pat. No. 7,867,931 to Apel et al discloses a lithium silicate glass ceramic with silicon dioxide composition of 64%-75% weight and lithium oxide composition of 13-17% weight producing lithium disilicate as the final product. They also describe a glass ceramic with a molar ratio of silicon dioxide to lithium oxide in the range of 2.3 to 2.5.

U.S. Pat. No. 8,042,358 to Schweiger et al discloses a lithium silicate glass ceramic with silicon dioxide composition of 65%-70% weight and lithium oxide composition of 14-16% weight producing lithium disilicate as the final product. In their specific process the raw materials such as carbonates, oxides and phosphates are prepared and melted in the range of 1300-1600° C. for 2 to 10 hours. They explain that in order to obtain a particularly high degree of homogeneity the glass melt obtained may be poured into water to form glass granulates and the glass granulates obtained are melted again.

For those skilled in the art it is understandable that the lithium oxide—silicon dioxide system has been extensively studied and several patents for dental glass ceramics have been granted in the last few years. However all the research so far falls in the range where lithium disilicate is formed as a final product and none of the references above disclose lithium silicate glass ceramic as a final product. For those skilled in the art it is evident that the type of crystal produced depends exclusively on the molar ratio of silicon dioxide to lithium oxide in the glass ceramic and not the additives or modifiers added to the mixture. This molar ratio controls the type of crystal formed in the final composition and furthermore give its name to the final glass ceramic.

Most of the existing patents in the dental field use the same basic components. The present invention uses germanium dioxide as a fundamental part of the formula. This oxide is broadly used in glass preparation for its good optical properties. The oxide has been well studied and has positive effects compared to common silicon glasses. It has been found that the addition of germanium oxide produces a melt with low viscosity, which facilitates the castability of the process and increases the thermal expansion and the refractive index of the resulting lithium silicate glass ceramic. More importantly, the addition of germanium dioxide increases the final density of the glass resulting in higher values of flexural strength than the lithium disilicate glasses free of germanium dioxide. U.S. Patent Application Publication No. 2004/0197738 to Ban et al discloses a process to make dental frame of zirconium-ytrium sintered ceramics and they describe dental porcelain with germanium oxide as a joint component different than the zirconium yttrium oxide frame. However germanium oxide is not used as a component of the framework ceramic network. It is used only in formulation of the ceramic joint and is just a part of a series of other oxides that can be joined to the framework material.

Due to the low silicon dioxide to lithium oxide molar ratio of 1.7 of the present invention, equivalent to 37% molar of lithium oxide (63% silicon dioxide) the ceramic has a lower melting point compared to the glass ceramic of the prior art. In addition, this new glass ceramic contains the lowest silicon dioxide weight percent compared to all of the noted prior art. Therefore, due to this specific composition of lithium oxide in the mixture, the type of resulting crystal after crystallization (lithium silicate) gives to the glass ceramic its own chemical and physical properties, which makes it completely distinguishable from the prior glass ceramics listed above. Due to

this distinguishable composition, the present glass ceramic has a lower melting temperature and can be made even lower with the addition of germanium oxide. Germanium oxide replaces silicon dioxide in the glass network, causing it to have a negative effect on the resulting melting point compared to a glass ceramic containing only silicon dioxide. Thus the processing and optimal melting temperature is in the range of 1100° C. to 1200° C. instead of 1200° C. to 1650° C. of the U.S. patents cited above and specifically compared to U.S. Pat. No. 6,514,893 to Schweiger et al. The glass ceramics listed in the prior art patents cannot be cast in the range of 1100° C. to 1200° C. because they are too viscous due to their high silicon dioxide content, therefore the processes disclosed in prior art patents with higher melting temperatures should be used. The present process will result in a more economical production because the energy employed for melting the glass is considerably lower and there are lower energy loses by radiation compared to the Schweiger process.

In addition to having a process with lower energy consumption, another significant improvement of the inventive process is related to the mixing and reaction of the components. In all of the previously cited prior art patents, the mix of the components is blended and melted at 1400 to 1650° C. and then cast or quenched in water. The quenched glass powder is dried, milled, and melted again in order to improve the homogeneity and the quality of the product. Surprisingly, it was found that the first melting and casting process can be avoided if one performs a calcination process on the mixture of raw materials to a temperature in the range of 700 to 800° C. without melting the components. At this stage, all the raw materials in the form of salts (like lithium carbonate as the source of lithium oxide, calcium carbonate as the source of calcium oxide, and di-ammonium phosphate as the source of phosphorous oxide) are decomposed, eliminating gases such carbon dioxide and ammonia, producing a ceramic powder free of gases. After cooling down, the calcined mix is milled again, producing a homogeneous powder with a very small particle size. The final step is melting and casting in the range of 1100° C. to 1200° C., resulting in a homogeneity of all the components. In addition, by eliminating the gases during the calcination process, the glass cast becomes bubble free, making this a significant advantage over the processes described in the prior art.

The present invention is also unique compared to those listed in the prior art due to its composition. The use of a low melting temperature is only possible with the present glass ceramic because of the low content of silicon dioxide and the high content of lithium oxide. This translates to a molar oxide ratio (SiO_2/Li_2O) below 2.0, (i.e., 1.7) in which only lithium silicate crystals are produced (SiO_2—Li_2O). In addition to the composition, the present invention implements a process for a glass ceramic that produces a homogeneous product and that can be used only with the specific formulation. This process cannot be used with the other listed glass ceramics due to the lower operating temperatures.

The present invention emphasizes that in the inventive glass ceramic the silicon dioxide and lithium oxide molar ratio content (SiO_2/Li_2O) is less than 2, specifically the oxide molar ratio is preferably about 1.7. This is specifically equivalent to 63% molar of silicon dioxide and 37% molar of lithium oxide, and specifically equivalent in the overall formulation of about 56% weight percent of all of the glass ceramic as silicon dioxide and 16.0% weight percent as lithium oxide and the remaining 28% composed of the oxide additives and modifiers. In all of the glass ceramic, only lithium silicate (Li_2O—SiO_2) crystals are produced as the final crystal phase product. During the heating process of the glass, the first crystals formed are stable lithium silicate and they remain stable through the end of the growing process. This means that there is no need for a third thermal process for producing the final crystal of lithium silicate making this an additional characteristic unique to the present invention. This new ceramic has softening temperature of about 700 to 800° C. and a linear thermal coefficient of expansion of about 12 to 12.5×10^{-6}/° C. as a final product and a composition yielding completely different chemical and physical properties compared to the prior art. This is easily demonstrated in commonly assigned U.S. patent application Ser. No. 12/592,825, paragraph [0012], FIG. **1** showing a XRD pattern diffraction where only lithium silicate crystals are present in the final product and paragraph [0013] where the glass ceramic has a percentage linear change of 0.55% measured at 500° C. and an equivalent coefficient of thermal expansion of 11.5×10^{-6}/° C.

The following is a list of non-patent references noted herein:

1. MARCUS P. BOROM et al, Strength And Microstructure In Lithium Disilicate Glass-Ceramics, J. Am. Ceram. Soc., September-October 1975, Vol. 58, No. 9-10, pp 385-391. The authors prepare lithum disilicate glass ceramics and measured the differences between the thermal expansion of the lithium disilicate with a value of 13×10^{-6}/° C. and lithium silicate with a value of 11.4×10^{-6}/° C. After the heat treatment above 800° C. the only phase present is lithium disilicate for a glass ceramic composition of 71.8% of silicon dioxide and 12.6 of lithium oxide.
2. R. A. EPPLER, Glass Formation And Recrystallization In The Lithium Metasilicate Region Of The System Li_2O—Al_2O_3—SiO_2, J. Am. Ceram. Soc., February 1963, Vol. 46, No. 2, pp 97-101.
3. F. A. HUMMEL, Thermal Expansion Properties Of Some Synthetic Lithia Minerals, J. Am. Ceram. Soc., August 1951, Vol. 34, No. 8, pp 235-239.
4. LANDOLT-BÖRNSTEIN (LB), Group IV Physical Chemistry—Phase Equilibria, Crystallographic And Thermodynamic Data For Intermediate Compounds in the Li_2O—SiO_2 System.
5. S. CLAUS et al, Phase Equilibria In The Li_4SiO_4—Li_2SiO_3 Region Of The Pseudobinary Li_2O—SiO_2, Journal of Nuclear Materials, Vol. 230, Issue 1, May 1996, pp 8-11.
6. HERMAN F. SHERMER, Thermal Expansion Of Binary Alkali Silicate Glasses, Journal of Research of the National Bureau of Standards, Vol. 57, No. 2, August 1956. The author prepares lithium silicate glasses with silicon oxide and lithium oxide molar ratio below 2.0 being lithium silicate with thermal expansion between 12 and 14.77×10^{-6}/° C. There is no lithium disilicate using this chemical molar composition.

SUMMARY OF THE INVENTION

The present invention relates to preparing an improved lithium silicate glass ceramic for the manufacture of blocks for dental appliance fabrication using a CAD/CAM process and hot pressing. The lithium silicate material has a chemical composition that is different from those reported in the prior art, especially because of the use of germanium dioxide in the formulas and its low silicon dioxide content. The softening points are close to the crystallization final temperature of 800° C. indicating that the samples will support the temperature process without shape deformation.

The initial components are chemical precursors, specifically aluminum hydroxide for aluminum oxide, boric acid for boron oxide, lithium carbonate for lithium oxide, ammonium hydrogen phosphate or calcium phosphate for phosphorus pentoxide, zirconium silicate or yttrium stabilized zirconia for zirconium oxide, calcium carbonate for calcium oxide, lithium fluoride for lithium oxide and fluoride, and potassium carbonate for potassium oxide. The remaining elements are single oxide precursors of silicon, cerium, titanium, tin, erbium, vanadium, germanium, samarium, niobium, yttrium, europium, tantalum, magnesium, praseodymium, and vanadium oxides.

The components are carefully weighed and then mechanically blended using a V-cone blender for about 5 to 10 minutes. Then in order to achieve uniform particle size of the components, the mixture undergoes a ball mill process for two hours. The powder obtained is put into large alumina crucibles and undergoes calcination to 800° C. for about 4 hours. In this stage the carbonate precursors, lithium carbonate, calcium carbonate, potassium carbonate, decompose releasing carbonic gas and producing the corresponding pure oxides, lithium oxide, calcium oxide and potassium oxide, respectively. In the same process the other chemical precursors, ammonium phosphate, aluminum hydroxide and boric acid also release nitrogen gases and water producing the corresponding pure oxides, phosphorous pentoxide, aluminum oxide and boron oxide, respectively. At this stage of calcination the original powder mix loses approximately 25% of its original weight due to the evaporation losses. Also, the first reactions between the pure oxides are taking place in this stage but there is never any melting of the components and no reaction takes place with the alumina crucible. After cooling down, the blend of components undergoes ball milling again, producing a homogeneous, gas free, fine powder with a particle size below 30 microns. The calcined powder can be safely stored in plastic containers for extended periods of time without any gas release and can be used anytime for the next step of the process.

In the final stage of the process the calcined powder is melted in a platinum crucible at a temperature of 1200° C. with a holding time of about 2 hours before casting. The melt with the appropriate viscosity is cast continuously over graphite molds. Surprisingly, the glass cast is bubble free due to the prior elimination of the gases during the calcination step. This constitutes a significant advantage over the processes described in the prior art. Due to the calcination process step, there is no need for a second re-melting process for improving homogeneity. The glass cast is then subjected to an annealing step followed by an intermediate crystallization step or a full crystallization step depending on what is desired as a final product.

Due to the specific molar ratio of silicon dioxide and lithium oxide (1.7/1) used in the present invention, the only preferred crystal structure formed is lithium silicate ($SiO_2.Li_2O$) in the intermediate or full crystallized product. Surprisingly it was found that in this invention, the crystal growth process can be momentarily stopped at any temperature interval between the ranges of 350° to 800° C. and then the crystal can continue growing by heating it again to reach the optimal size at 800° C. Above 800° C. the sample starts melting and the reverse process of dissolving the crystals in the glass matrix takes place.

Thus in the present invention, the intermediate crystallization process step is easily controlled by stopping the heating process at 600° C. and cooling down to room temperature. It can then be heated again to 800° C. for achieving the full crystallized product. Thus if one takes the intermediate block material of lithium silicate, after the thermal heat process from room temperature to 600° C., it can be milled to a dental restoration using conventional CAD/CAM devices and then it can be heated up again to 800° C. continuing towards maximum crystal growth and achieving the optimal physical properties. Surprisingly, the same formulation, after a thermal process from room temperature to 800° C., can be easily hot pressed in the range of 800-840° C. using conventional all ceramic dental investments and commercial press furnaces (i.e Whip Mix Pro-Press 100). For the hot press process, the dental restoration is milled in a wax block, followed by investing the wax pattern using commercial all ceramic investments. After firing the investment, the wax is burned out, allowing the cavity of the restoration to become available to fill with the ceramic. After hot pressing the restoration achieves the optimal physical properties.

The same formulation produces the same lithium silicate crystalline phase through all the thermal process steps and the dental restoration can be optimally achieved by using either CAD/CAM or hot press techniques. Being able to achieve this with the same formulation is a unique and advantageous characteristic over the prior art.

BRIEF DESCRIPTION OF THE DRAWINGS

The aforementioned objects and advantages of the present invention, as well as additional objects and advantages thereof, will be more fully understood herein after as a result of a detailed description of a preferred embodiment when taken in conjunction with the following drawings in which:

FIG. **1** is an XRD diffraction pattern of a sample of the invention after the intermediate crystallization step (from room temperature to 600° C.) showing the presence of lithium silicate as a main constituent phase in the glass ceramic composition;

FIG. **2** is an XRD diffraction pattern of a sample of the invention after the full crystallization step (from room temperature to 800° C.) showing the presence of lithium silicate as a main constituent phase in the glass ceramic composition. Because the molar ratio of SiO_2/Li_2O is between 1.7 to 1.9, the crystallized phase of the final material shows the presence of only lithium silicate and no lithium disilicate;

FIG. **3** is an XRD diffraction pattern of a sample of this invention after hot pressing in the interval of 800° C. to 840° C. showing the presence of lithium silicate as a main constituent phase in the glass ceramic composition. Because the molar ratio of SiO_2/Li_2O is between 1.7 to 1.9, the crystallized phase of the final material shows the presence of lithium silicate and no lithium disilicate; and

FIG. **4** is a graphical illustration of a dilatometric measurement of a sample of the invention resulting from full crystallization. The softening temperature of the intermediate step is lower than the temperature after full crystallization. This is due to the crystal growth after heating the glass in the intermediate stage from room temperature to 800° C.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The prior art materials are based on the formation of lithium disilicate materials. A principal object of the present invention is to prepare a controlled lithium silicate glass ceramic using in the formulation a specific silicon dioxide and lithium oxide molar ratio with excellent physical properties for manufacturing dental restorations. The glass material subjected to a heat treatment produces an optimal lithium silicate crystal forming a glass ceramic product with out-

standing mechanical properties, excellent optical properties, a very good chemical solubility, little contraction and high flexural strength values.

The lithium silicate of the present invention preferably comprises the following components and compositions:

Component	weight % composition minimum	maximum
SiO_2	53.0	57.0
Al_2O_3	3.0	5.0
K_2O	3.0	5.0
CaO	0.0	1.0
B_2O_3	0.0	2.0
CeO_2	0.0	1.0
MgO	0.0	1.0
Fluorine	0.0	1.0
Li_2O	14.0	17.0
ZrO_2	4.0	5.0
TiO_2	0.0	3.0
P_2O_5	2.0	3.0
SnO	0.0	1.0
Er_2O_3	0.0	2.0
V_2O_5	0.0	1.0
GeO_2	0.5	8.0
Ta_2O_5	0.0	3.0
Sm_2O_3	1.0	6.0
Pr_2O_3	0.0	1.0
Eu_2O_3	0.0	2.0
Y_2O_3	0.0	5.0
Nb_2O_5	0.0	1.0

The invention is explained in more detail below with the following examples:

The sample preparation and its elemental oxide composition are listed in Table 1.

TABLE 1

	Components % weight. Example 1	Example 2	Example 3	Example 4	Example 5
SiO_2	55.03	56.19	56.21	56.21	53.88
Al_2O_3	4.09	4.18	4.18	4.18	3.11
K_2O	4.42	4.52	4.52	4.52	3.44
CaO	0.94	0.96	0.96	0.96	0.00
B_2O_3	1.58	1.61	1.61	1.61	0.00
CeO_2	0.21	0.65	0.34	0.41	0.63
MgO	0.22	0.23	0.23	0.23	0.00
Fluorine	0.49	0.50	0.50	0.50	0.00
Li_2O	15.81	16.14	16.15	16.15	14.81
ZrO_2	4.70	4.79	4.80	4.80	4.88
TiO_2	2.40	0.80	0.80	0.80	0.63
P_2O_5	2.52	2.58	2.58	2.58	2.94
SnO	0.22	0.07	0.13	0.12	0.00
Er_2O_3	0.37	0.76	0.36	0.21	1.26
V_2O_5	0.39	0.22	0.26	0.11	0.03
GeO_2	0.90	0.92	0.92	0.92	7.75
Ta_2O_5	0.07	0.15	0.22	0.01	0.00
Sm_2O_3	2.03	4.09	4.07	4.09	5.71
Pr_2O_3	0.03	0.33	0.04	0.00	0.88
Eu_2O_3	0.00	0.00	0.00	1.25	0.05
Y_2O_3	3.13	0.11	0.61	0.36	0.00
Nb_2O_5	0.46	0.22	0.53	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00
	Example 6	Example 7	Example 8	Example 9	Example 10
SiO_2	54.08	54.49	56.17	53.49	56.19
Al_2O_3	3.12	3.86	4.18	3.98	4.18
K_2O	3.45	4.20	4.52	4.30	4.52
CaO	0.00	0.00	0.96	0.92	0.96
B_2O_3	0.00	0.00	1.61	1.53	1.61
CeO_2	0.95	0.64	0.00	0.20	0.62

TABLE 1-continued

	Components % weight.				
MgO	0.00	0.00	0.23	0.22	0.23
Fluorine	0.00	0.00	0.50	0.48	0.50
Li_2O	14.85	15.25	16.15	15.37	16.14
ZrO_2	4.89	4.88	4.80	4.56	4.79
TiO_2	0.63	0.64	0.80	0.78	0.80
P_2O_5	2.95	2.97	2.58	2.45	2.58
SnO	0.00	0.00	0.00	0.00	0.07
Er_2O_3	1.52	1.28	0.05	0.16	0.61
V_2O_5	0.06	0.04	0.00	0.48	0.15
GeO_2	7.77	7.70	0.92	0.87	0.92
Ta_2O_5	0.00	0.00	2.33	0.00	0.18
Sm_2O_3	4.82	3.34	1.83	4.90	4.05
Pr_2O_3	0.90	0.72	0.00	0.23	0.24
Eu_2O_3	0.00	0.00	0.05	0.00	0.00
Y_2O_3	0.00	0.00	2.33	4.90	0.24
Nb_2O_5	0.00	0.00	0.00	0.18	0.45
TOTAL	100.00	100.00	100.00	100.00	100.00

A particularly preferred lithium silicate material as described in the examples 1 to 10 comprises 53 to 59 wt % of SiO_2, 14 to 19% wt of Li_20 and 1 to 9% of GeO_2, where after nucleation only lithium silicate is formed and then after complete crystal growth only lithium silicate crystals are formed.

The lithium silicate material of this invention is preferably produced by a process which comprises the following steps:

(a) A mix of the precursors of the final components of the table 1, are blended together for 10 to 30 min until a mechanical mix is obtained.

(b) The mix is ball milled dry or wet using zirconia media for about 1 to 2 hours to homogenize the components and achieve almost the same particle size in all the components.

(c) The sample is calcined at 800° C. for about 1 to 4 hours in order to decompose the precursors to their primary oxides and eliminate any possibility of formation of gas after the process.

(d) Ball-mill the sample of step (c) in order to produce a powder with an average particle size below 30 microns.

(e) The powder of step (d) is melted in a platinum crucible at a temperature between 1100 to 1200° C. for 1 to 2 hours. It is then poured into cylindrical or rectangular graphite molds and cooled down to room temperature.

(f) The glass ceramic of step (e) is then subjected to an intermediate crystal growth process at a temperature of from room temperature to 600° C. for 10 to 60 min. The growth of the lithium silicate crystals is temporarily stopped for the desired intermediate size by cooling the glass ceramic to room temperature.

(g) The glass ceramic of step (f) is subjected to a single step heating cycle from room temperature to 800° C. to achieve full crystallization.

(h) For use in a CAD-CAM milling device, the dental restoration is made using a block after intermediate process step (f). After milling, the restoration is heated again from 350° C. to 800° C. or to full crystallization step (g) where the optimal lithium silicate crystal growth in the glass ceramic is achieved in a single step program.

(i) For an alternative hot pressing technique, the sample after [step (g)] is pressed into a dental restoration at a temperature of 800-840° C., where the optimal lithium silicate crystal growth in the glass ceramic is achieved.

Coefficient of Thermal Expansion and Softening Point

The percentage linear change vs. temperature was measured using an Orton dilatometer. The coefficient of thermal expansion at 500° C. and the softening point were calculated

for all the samples. For this purpose a rectangular rod of approximately 2 inches long was cast and then subjected to the intermediate crystallization cycle at 600° C. for 40 min. After this process the rod is cut into two parts. One part is used for measuring transition temperature, softening point temperature, and coefficient of thermal expansion of that process step. The second part is fully crystallized at 800° C. for about 10 minutes and is used for measuring the same properties. It is expected that after the crystallization step, the softening temperature point increases for the samples due to the formation of larger lithium silicate crystals. Test results are displayed in Table 2.

Flexural Strength.

Biaxial flexural strength tests (MPa) were performed following ISO-6872 procedures. Ten round samples were cut, grinded gradually and polished to a mirror finish in the intermediate stage or step (f). The samples were then fully crystallized in a single stage program from 350° C. to 800° C. for 10 minutes. Then the biaxial flexural strength was measured. For the hot pressing technique the glass ceramic of sample of step (g) is hot pressed into round discs in the interval of 800 to 840° C. Then the discs are grinded gradually and polished to a mirror finish, heated as a simulated glaze cycle, and tested. Test results expressed in MPa are displayed in Table 2.

Chemical Solubility.

A chemical solubility test was performed according to ISO-6872. Ten discs samples subjected to step (g) are placed in a glass flask with an aqueous solution of 4% (V/V) of acetic acid analytical grade (Alfa Aesar). The flask is heated to a temperature of 80+/−3° C. for 16 hours. The change in weight before and after the test is determined and then the chemical solubility expressed as μg/cm^2 is calculated and shown in Table 2.

TABLE 2

Physical Properties of the Lithium silicate glass ceramic.

	Example #2	Example #3	Example #4	Example #5	Example #8
Softening temperature, ° C., Intermediate stage at 600° C.	689	618	690	766	711
Softening temperature, ° C., crystallized sample at 800° C.	727	744	717	789	724
Coefficient of expansion, X10^{-6}/° C. Crystallized sample at 800° C.	11.81	12.58	12.27	11.30	11.61
Flexural strength, MPa, Crystallized at 800° C.	350 +/− 28	402 +/− 56	359 +/− 40	365 +/− 60	370 +/− 50
Flexural strength, MPa Hot pressed sample	393 +/− 48	423 +/− 61	523 +/− 39	345 +/− 20	397 +/− 57
Chemical Solubility, μg/cm^2 Crystallized sample at 800° C.	72	58	65	39	58

The preferred range composition (in % wt) of this glass ceramic material is the following:

TABLE 5

Preferred Range of Composition Components

	weight % composition	
Component	minimum	maximum
SiO_2	53.5	56.2
Al_2O_3	3.1	4.2
K_2O	3.4	4.5
CaO	0.0	1.0
B_2O_3	0.0	1.6
CeO_2	0.0	1.0

TABLE 5-continued

Preferred Range of Composition Components

	weight % composition	
Component	minimum	maximum
MgO	0.0	0.2
Fluorine	0.0	0.5
Li_2O	14.8	16.1
ZrO_2	4.6	4.9
TiO_2	0.6	2.4
P_2O_5	2.5	3.0
SnO	0.0	0.2
Er_2O_3	0.1	1.5
V_2O_5	0.0	0.5
GeO_2	0.9	7.8
Ta_2O_5	0.0	2.3
Sm_2O_3	1.8	5.7
Pr_2O_3	0.0	0.9
Eu_2O_3	0.0	1.3
Y_2O_3	0.0	4.9
Nb_2O_5	0.0	0.5

One preferred example of this material has the following specific composition:

TABLE 6

Preferred Composition

Component	Weight %
SiO_2	55.74
Al_2O_3	4.15
K_2O	4.48

TABLE 6-continued

Preferred Composition

Component	Weight %
CaO	0.95
B_2O_3	1.60
MgO	0.23
Fluorine	0.50
Li_2O	16.01
ZrO_2	4.76
TiO_2	0.80
P_2O_5	2.56
GeO_2	0.91
Coloring oxides	7.32

Having thus disclosed a number of embodiments of the formulation of the present invention, including a preferred range of components, a preferred formula thereof and a preferred fabrication process, those having skill in the relevant arts will now perceive various modifications and additions. Therefore, the scope hereof is to be limited only by the appended claims and their equivalents.

I claim:

1. A lithium silicate ceramic glass made from a composition mixture comprising:

53% to 59% wt of SiO_2;

14% to 19% wt of Li_2O;

1% to 9% wt of GeO_2; and

coloring oxides.

2. The lithium silicate ceramic glass recited in claim **1** wherein said composition mixture also comprises at least one of the following components: Al_2O_3, K_2O, B_2O_3, CaO, MgO, CeO_2, P_2O_5, ZrO_2, TiO_2, Er_2O_3, V_2O_5, Ta_2O_5, Sm_2O_3, Pr_2O_3, and Eu_2O_3.

3. A lithium silicate ceramic glass made from a composition mixture comprising:

53% to 59% wt of SiO_2;

14to 19% wt of Li_2O;

1% to 9% wt of GeO_2;

wherein the molar ratio of SiO_2/Li_2O is between 1.8 and 1.9.

4. The lithium silicate ceramic glass recited in claim **3** wherein said composition mixture also comprises at least one of the following components:

Al_2O_3, K_2O, B_2O_3, CaO, MgO, CeO_2, P_2O_5, ZrO_2, TiO_2, Er_2O_3, V_2O_5, Ta_2O_5, Sm_2O_3, Pr_2O_3, and Eu_2O_3.

5. A lithium silicate dental ceramic glass article comprising:

silicon dioxide (SiO_2), lithium oxide (Li_2O), and germanium oxide (GeO_2), wherein a molar ratio of SiO_2/Li_2O is between 1.8 and 1.9.

6. The lithium silicate dental ceramic glass article recited in claim **5**, wherein the article is fully crystallized and a crystal structure of the article comprises lithium silicate (Li_2SiO_3).

7. The lithium silicate dental ceramic glass article recited in claim **5**, wherein the article is fully crystallized and a crystal structure of the article comprises only lithium silicate (Li_2SiO_3).

* * * * *