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(54) Title: METHOD FOR THE PRODUCTION OF A FORM BODY COMPRISING OR CONTAINING A LITHIUM SILICATE GLASS CERAMIC AS WELL AS FORM BODIES

(57) Abstract: The invention relates to a method for the production of a medical form body comprising or containing a lithium silicate glass ceramic. To allow the strength of the form body to be increased compared to the prior art, it is proposed that in a preform body comprising or containing a lithium silicate glass ceramic with a geometry that corresponds to the form body a surface compressive stress is created by replacement of lithium ions with alkali ions of greater diameter, wherein after substitution of the ions the preform body is used as the form body.



WO 2016/124486 A1

5 **Description**

Method for the production of a form body comprising or containing a lithium silicate glass ceramic as well as form bodies

10

The invention relates to a method for the production of a medical, preferably dental, form body, or part thereof comprising or containing lithium silicate glass ceramic, in particular a bridge, crown, cap, inlay, onlay or veneer. The invention also relates to a form body in the form of a medical, especially dental, object or a part thereof, in particular a bridge,
15 crown, cap, inlay, onlay or veneer, comprising or containing a lithium silicate glass ceramic.

The use of lithium silicate glass ceramic for blanks for the manufacture of dental restorations has proven itself in dental technology for reasons of strength and
20 biocompatibility. An advantage is that if a lithium silicate blank contains lithium metasilicate as the main crystal phase, then machine working is possible without difficulty, without high tool wear. Upon subsequent heat treatment, in which the product is transformed into a lithium disilicate glass ceramic, a high strength results. Good optical properties and an adequate chemical stability also result. Corresponding methods are
25 disclosed, for example, in DE 197 50 794 A1 or DE 103 36 913 B4.

To achieve a high strength while at the same time good translucency, it is known for at least one stabilizer from the group zirconium oxide, hafnium oxide or a mixture thereof, in particular zirconium oxide, to be added to the starting materials in the form of lithium
30 carbonate, quartz, aluminum oxide etc., i.e., the usual starting components. Attention is drawn here, for example, to DE 10 2009 060 274 A1, WO 2012/175450 A1, WO 2012/175615 A1, WO 2013/053865 A2 or EP 2 662 342 A1.

The object of the present invention is to develop a method of the type described above

such that simple process technology measures allow the strength of the form body to be increased compared to the prior art.

5 The object is substantially met according to the invention in that in a preform body comprising or containing a lithium silicate glass ceramic with a geometry that corresponds to the form body a surface compressive stress is created by replacement of lithium ions with alkali ions of greater diameter, such as potassium ions, sodium ions and/or rubidium ions, wherein after substitution of the ions the preform body is used as the form body.

10 The term form body thereby embraces a possible subsequent working, for example in the dental applications veneering of a crown or bridge.

Surprisingly, it was found that when the lithium ions present in the preform body of lithium silicate glass ceramic were replaced by the larger alkali ions, a pre-stress and thus
15 a surface compressive stress are created to a degree that a substantial increase in strength results.

It was also surprisingly found that the corrosion resistance increased at the same time. It was thus found that in addition to an increase in strength through ion exchange, wherein
20 flexural strengths of, in particular, more than 500 MPa are attained, as determined using the three-point bending measurement method specified in DIN EN ISO 6872-2009-01, an improvement in chemical resistance is achieved which – also determined by the method given in DIN EN ISO 6872-2009-1 – exhibited a chemical solubility of $< 95 \mu\text{g} \times \text{cm}^{-2}$.

25 The use of Na, K, Cs and/or Rb as alkali ions is preferred to generate the surface compressive stress.

In particular it is intended for the preform body to be annealed in a melt containing alkali ions. The melt may contain ions of one alkali metal or of a number of alkali metals.

30

It is thereby in particular provided for the melt to contain elements, dissolved in the melt, that impart color to the preform body. These may be one or more lanthanides with an atomic number between 58 and 70, preferably cerium, praseodymium, terbium or erbium.

However, vanadium, manganese, iron, yttrium or antimony may also be used to provide color.

5 The elements are in particular in salt form, so that they are dissolved in the melt containing alkali ions, so that the color-imparting elements diffuse from the liquid phase into the glass ceramic.

10 In particular the required exchange between lithium ions and potassium ions is ensured if the preform body is annealed in a melt containing potassium ions. Preferred salt melts are KNO_3 , KCl or K_2CO_3 salt melts.

15 The invention is characterized in a preferred manner in that the preform body is annealed in a melt containing potassium ions, in particular a melt containing KNO_3 , KCl or K_2CO_3 , or in a melt containing sodium ions, in particular in a melt containing NaNO_3 , or in a melt containing a mixture of potassium ions and sodium ions, in particular in a ratio of 50:50 mol%, preferably in a melt containing NaNO_3 and KNO_3 .

20 The required ion exchange in the surface region is particularly good when the preform body is annealed at a temperature $T \geq 300^\circ\text{C}$, in particular $350^\circ\text{C} \leq T \leq 600^\circ\text{C}$, preferably $430^\circ\text{C} \leq T \leq 530^\circ\text{C}$, for a time $t \geq 5$ minutes, in particular $0.5 \text{ h} \leq t \leq 10 \text{ h}$, especially preferred $3 \text{ h} \leq t \leq 8 \text{ h}$.

25 Shorter annealing times in the region of up to 30 minutes are in principle sufficient to achieve the desired surface compressive stress in the surface region. If, however, a strengthening in the form body down to a depth of 20 μm or more is desired, then longer annealing times of, for example, 6 or 10 hours are required, depending on the annealing temperature.

30 Independently thereof, the form body available after annealing, in particular tooth replacement, is not subjected to a further temperature treatment, or if so then the temperature is below 200°C .

In a preferred embodiment, the preform body is fabricated from a glass melt, which as starting components contains at least SiO_2 , Al_2O_3 , Li_2O , K_2O , at least one nucleating

agent, such as P_2O_5 , and at least one stabilizer such as ZrO_2 .

The invention is also characterized in a way to be emphasized in that the lithium ions are not only replaced by larger alkali ions, in particular potassium and/or sodium ions, but in that at least one dissolved stabilizer, in the form of ZrO_2 , is contained in the glass phase of the form body to increase strength in the starting substance, wherein the preferred percentage by weight lies in the range 8 – 12, relative to the starting composition.

Prior to the ion exchange the preform body has the geometry of the form body to be provided such as a bridge, crown, cap, inlay, onlay or veneer. The preform body may – as is usual in the dental field – be subjected to glaze firing before the ion exchange is carried out.

The invention is characterized in particular in that the preform body is produced from a glass melt of the following composition in percentage by weight:

- SiO_2 50 – 80, preferably 52 – 70, especially preferred 56 – 61
- nucleating agent such as
 - P_2O_5 0.5 – 11, preferably 3 – 8, especially preferred 4 – 7
- Al_2O_3 0 – 10, preferably 0.5 – 5, especially preferred 1.5 – 3.2
- Li_2O 10 – 25, preferably 13 – 22, especially preferred 14 – 21
- K_2O 0 – 13, preferably 0.5 – 8, especially preferred 1.0 – 2.5
- Na_2O 0 – 1, preferably 0 – 0.5, especially preferred 0.2 – 0.5
- ZrO_2 0 – 20, preferably 4 – 16, in particular 6 – 14, especially preferred 8 – 12
- CeO_2 0 – 10, preferably 0.5 – 8, especially preferred 1.0 – 2.5
- Tb_4O_7 0 – 8, preferably 0.5 – 6, especially preferred 1.0 – 2.0
- optionally an oxide or a number of oxides of an earth alkali metal or a number of earth alkali metals of the group magnesium, calcium, strontium and barium
 - 0 – 20, preferably 0 – 10, especially preferred 0 – 5,
- optionally an oxide or a number of oxides from the group boron oxide, tin oxide and zinc oxide
 - 0 – 10, preferably 0 – 7, in particular 0 – 5,

wherein the total sum is 100% by weight.

“Optionally an oxide or a number of oxides” means that it is not absolutely necessary for one or a number of oxides to be contained in the glass melt.

5

In particular the preform body has the following composition in percentage by weight:

SiO ₂	58.1 ± 2.0
P ₂ O ₅	5.0 ± 1.5
Al ₂ O ₃	4.0 ± 2.5
Li ₂ O	16.5 ± 4.0
K ₂ O	2.0 ± 0.2
ZrO ₂	10.0 ± 0.5
CeO ₂	0-3, preferably 1.5 ± 0.6
Tb ₄ O ₇	0-3, preferably 1.2 ± 0.4,
Na ₂ O	0 – 0.5, preferably 0.2 – 0.5

wherein the total sum is 100% by weight.

10

The invention is characterized in that a blank is formed from the glass melt during cooling or after cooling to room temperature, with the said blank subjected to at least a first heat treatment W1 at a temperature T_{W1} over a time period t_{W1} , wherein $620\text{ }^{\circ}\text{C} \leq T_{W1} \leq 800\text{ }^{\circ}\text{C}$, in particular $650\text{ }^{\circ}\text{C} \leq T_{W1} \leq 750\text{ }^{\circ}\text{C}$, and/or $1\text{ minute} \leq t_{W1} \leq 200\text{ minutes}$, preferably
15 $10\text{ minutes} \leq t_{W1} \leq 60\text{ minutes}$. The preform body is derived from the blank / heat-treated blank.

20

The first heat-treatment phase results in nucleation and formation of lithium metasilicate crystals. A corresponding lithium silicate glass ceramic blank can be worked without difficulty, with minimal wear of the tool. A corresponding blank can also be pressed into a desired geometry.

25

In particular to achieve a final crystallization, in particular to form lithium disilicate crystals / transform the metasilicate crystals into disilicate crystals, it is provided that after the first heat treatment W1 the lithium silicate glass ceramic blank is subjected to a second

heat treatment W2 at a temperature T_{W2} over a time period t_{W2} , wherein $800^{\circ}\text{C} \leq T_{W2} \leq 1040^{\circ}\text{C}$, preferably $800^{\circ}\text{C} \leq T_{W2} \leq 900^{\circ}\text{C}$, and/or $2 \text{ minutes} \leq t_{W2} \leq 200 \text{ minutes}$, preferably $3 \text{ minutes} \leq t_{W2} \leq 30 \text{ minutes}$.

- 5 The heat treatment steps leading to a pre-crystallization / final crystallization preferably have the following temperature values and heating rates. With regard to the first heat treatment W1 this is in particular performed in two stages, wherein a first holding stage lies between 640°C and 680°C and a second holding stage lies between 720°C and 780°C . In each stage the heated molded part is held for a period of time, in the first stage
10 preferably between 35 and 45 minutes, and in the second stage preferably between 15 and 25 minutes.

- After the preform body has been derived from the blank, through grinding or milling, either after the first heat treatment step, or after the second heat treatment step, preferably
15 however after the second heat treatment step, i.e., it has the geometry of the form body to be produced, without generally requiring further working, the corresponding body, referred to as preform body, is annealed in a salt melt containing alkali ions, in particular potassium ions, to achieve the desired surface compressive stress. An annealing in a salt melt containing sodium ions, or a mixture of sodium ions and potassium ions is also
20 possible.

- The salt melt may contain color-imparting additives, wherein these in particular may be salts of one or more of the lanthanides from cerium to ytterbium (atomic numbers 58 to 70) and/or one or a number of salts of elements of the group vanadium, manganese, iron,
25 yttrium and antimony.

- After removal from the salt melt, cooling and the removal of any residue of the salt melt and to a certain extent necessary working of the form body so derived, this can be used to the extent desired, in particular as a dental restoration. As a result of the increase in
30 strength, the form body may be a multi unit bridge.

Specimens of corresponding form bodies, upon testing, were found to have flexural strength values above 400 MPa, in particular above 500 MPa. The values were determined using the three-point bending method given in DIN EN ISO 6872:2009-1.

In the hydrolysis test specified in DIN EN ISO 6872:2009-1 they had a chemical solubility of $< 100 \mu\text{g} \times \text{cm}^{-2}$. Consequently, the method according to the invention not only increases the strength of the form body, it also increases its resistance to corrosion.

5

A form body of the aforementioned type is characterized in that the form body has a surface compressive stress through the substitution of alkali ions such as Na, K, Cs and/or Rb, in particular potassium ions, for lithium ions.

10 In particular it is provided for the form body to be produced from a glass melt of the following composition in percentage by weight:

- SiO_2 50 – 80, preferably 52 – 70, especially preferred 56 – 61
 - nucleating agent such as
 - 15 P_2O_5 0.5 – 11, preferably 3 – 8, especially preferred 4 – 7
 - Al_2O_3 0 – 10, preferably 0.5 – 5, especially preferred 1.5 – 3.2
 - Li_2O 10 – 25, preferably 13 – 22, especially preferred 14 – 21
 - K_2O 0 – 13, preferably 0.5 – 8, especially preferred 1.0 – 2.5
 - Na_2O 0 – 1, preferably 0 – 0.5, especially preferred 0.2 – 0.5
 - 20 - ZrO_2 0 – 20, preferably 4 – 16, in particular 6 – 14, especially preferred 8 – 12
 - CeO_2 0 – 10, preferably 0.5 – 8, especially preferred 1.0 – 2.5
 - Tb_4O_7 0 – 8, preferably 0.5 – 6, especially preferred 1.0 – 2.0
 - optionally an oxide or a number of oxides of an earth alkali metal or a
 - 25 number of earth alkali metals of the group magnesium, calcium, strontium and barium
 - 0 – 20, preferably 0 – 10, especially preferred 0 – 5,
 - optionally an oxide or a number of oxides from the group boron oxide, tin oxide and zinc oxide
 - 30 0 – 10, preferably 0 – 7, in particular 0 – 5,
- wherein the total sum is 100% by weight.

“Optionally one oxide or a number of oxides” means that it is not essential for one or more oxides to be present in the glass melt.

The preform body in particular has the following composition in percentage by weight:

SiO ₂	58.1 ± 2.0
P ₂ O ₅	5.0 ± 1.5
Al ₂ O ₃	4.0 ± 2.5
Li ₂ O	16.5 ± 4.0
K ₂ O	2.0 ± 0.2
ZrO ₂	10.0 ± 0.5
CeO ₂	0-3, preferably 1.5 ± 0.6
Tb ₄ O ₇	0-3, preferably 1.2 ± 0.4,
Na ₂ O	0 – 0.5, preferably 0.2 – 0.5

5 wherein the total sum is 100% by weight.

Corresponding form bodies are characterized by a high strength. At the same time the starting composition results in a translucent product that has a high chemical resistance.

10 According to the invention the glass phase of the form body lies in the range 20-65% by volume, in particular 40-60% by volume.

The invention is characterized consequently by a form body in which the percentage by volume of the lithium silicate crystals lies in the range 35-80, in particular in the range 40-
15 60. Here, lithium silicate crystals refers to the sum of lithium disilicate crystals, lithium metasilicate crystals and lithium phosphate crystals.

In particular the form body is characterized in that the percentage of the alkali ions replacing the lithium ions, in particular with the use of potassium ions, starting from the
20 surface extending to a depth of 10 µm is in the range 5 – 20% by weight. At a depth of 8 – 12 µm from the surface the alkali ion percentage should be in the range 5 – 10% by weight. At a layer depth between 12 and 14 µm from the surface the percentage of alkali ions should be in the range 4 – 8% by weight. At a depth from the surface of between 14 and 18 µm the percentage of alkali ions is in the range 1 – 3% by weight. The percentage
25 by weight of the alkali ions decreases from layer to layer.

As mentioned, with the values in this instance the percentage by weight of the alkali ions present in the preform body is not taken into consideration. The numerical values hold in particular for potassium ions.

5

Further details, advantages and characteristics of the invention are derived not just from the claims, or from the characteristics to be drawn from these – alone and/or in combination – but also from the examples below.

10 For all tests at least the raw materials, such as lithium carbonate, quartz, aluminum oxide and zirconium oxide, were mixed in a drum mixer, until a uniform mass was reached when assessed visually. The compositions according to data supplied by the manufacturers used in the examples are given below.

15 The following apply in principle for the examples below:

The mass was melted in a crucible resistant to high temperature made from a platinum alloy at a temperature of 1500 °C for 5 hours. The melt was then poured into molds to derive rectangular bodies (blocks). The blocks then underwent a two-stage heat treatment referred to as a first heat treatment step to form lithium metasilicate crystals as the main
20 crystal phase (1st treatment step). The blocks were heated at a heating rate of 2 K/minute to 660 °C in the first heat treatment stage W1 and held at that temperature for 40 minutes. They were then heated further to 750 °C at a heating rate of 10 K/minute. The specimens were then held at this temperature for 20 minutes. This heat treatment influences
25 nucleation and results in the formation of lithium metasilicate crystals.

The blocks were then subjected to a second heat treatment step W2 (2nd treatment step) to form lithium disilicate crystals as the main crystal phase. In this heat treatment step the blocks were maintained at a temperature T_2 for a period of time t_2 . The corresponding
30 values are given below. The blocks were then cooled to room temperature.

Bending rods (specimens) were then derived from the cooled blocks through machine working (3rd treatment step), specifically through grinding of the blocks. The bending rods had a length of 15 mm, a width of 4.1 mm and a height of 1.2 mm. The edges of some

of the specimens were rounded off through the use of silicon carbide abrasive paper with a grit of 1200. A Struers Knuth rotor grinder was used for grinding. The specimens were ground on the sides (4th treatment step). Here too a SiC abrasive paper with a grit of 1200 was used. A few further specimens were also subjected to glaze firing (5th treatment step) without applying material. This glaze firing, designated the third heat treatment step, was carried out at a temperature T_3 for a holding period t_3 . The purpose of the glaze firing is to seal any cracks on the surface.

The three-point bending measurements were carried out as specified in DIN EN ISO 6872:2009-01. The specimens (rods) were mounted on two supports at a distance of 10 mm apart. A test stamp was used for the test and had a tip with a radius of 0.8 mm acting on the specimen.

The specimens were also subjected to a hydrolysis test as specified in DIN EN ISO 6872:2009-01.

Example 1 (lithium silicate glass ceramic according to the invention)

The following starting composition (in percentage by weight) was used to carry out a number of test series in accordance with the instructions of the manufacturer, to derive lithium silicate glass and therefrom lithium silicate glass ceramic material.

SiO ₂	58.1 – 59.1
P ₂ O ₅	5.8 – 5.9
Al ₂ O ₃	1.9 – 2.0
Li ₂ O	18.5 – 18.8
K ₂ O	1.9 – 2.0
ZrO ₂	9.5 – 10.5
CeO ₂	1.0 – 2.0
Tb ₄ O ₇	1.0 – 1.5
Na ₂ O	0 – 0.2

The glass phase lay in the range 40 – 60% by volume.

a) Test series #1

A total of 20 rods were produced first, and subjected to treatment steps 1 to 5. The final crystallization (second heat treatment step) was carried out at a temperature $T_2 = 830\text{ }^{\circ}\text{C}$ for a holding time $t_2 = 5$ minutes. The glaze firing (treatment step 5) was carried out at a temperature $T_3 = 820\text{ }^{\circ}\text{C}$ with a holding period $t_3 = 4$ minutes.

5

Ten of these rods were included in the three-point bending test without further treatment. The mean value obtained was 322 MPa.

10 The remaining ten rods were then annealed in a technically pure KNO_3 salt bath at a temperature of $480\text{ }^{\circ}\text{C}$ for 1 hour. The rods were then removed from the melt. The remaining melt residue was removed using warm water. The three-point bending measurements were then carried out as explained above. The mean three-point bending value was 750 MPa.

15 b) Test series #2

In a second test series 20 rods were derived by the method used for test series #1. The ten rods that were included in the three-point bending measurements immediately after glaze firing had a mean three-point flexural strength value of 347 MPa. The remaining 10 rods
20 were then annealed in a technically pure KNO_3 melt at a temperature of $480\text{ }^{\circ}\text{C}$ for 10 hours. This yielded a mean flexural strength of 755 MPa.

c) Test series #3

25 The chemical solubility of rods derived by the same method as for the first test series was determined as specified in DIN EN ISO 6872:2009-01, both for rods that were annealed in a KNO_3 melt and for rods without such annealing. The rods which were not annealed in the potassium ion melt had a starting value of $96.35\text{ }\mu\text{g} \times \text{cm}^{-2}$.

The chemical solubility of the annealed rods was $90.56\text{ }\mu\text{g} \times \text{cm}^{-2}$.

30

d) Test series #4

Rods were then derived from the aforementioned starting materials but were only subjected to treatment steps 1, 2 and 3, so that there was no rounding off of the edges, or

polishing or glaze firing. Of the 20 rods produced, the three-point flexural strength was measured for 10 of them. The mean value obtained was 187 MPa. The remaining 10 rods were then annealed in a technically pure KNO_3 salt melt at a temperature of 580 °C for 10 hours. The mean three-point flexural strength was 571 MPa.

5

e) Test series #5

Twenty rods of a lithium silicate material of the aforementioned composition were prepared, wherein treatment steps 1 to 4 were carried out, i.e., without glaze firing. The mean flexural strength value for 10 of the tested rods not annealed was 233 MPa. The remaining 10 rods were then annealed in a NaNO_3 melt for 20 minutes at 480 °C. The rods had a flexural strength of 620 MPa.

The examples showed that all specimens had an increase in strength of more than 100%, irrespective of whether the rods were annealed in an alkali ion melt with a good mechanical preparation (test series a), b), e)) or without a good mechanical preparation (test series d)).

With respect to the deviations in the starting values, i.e., without annealing, it should be noted that the specimens were derived from different batches of starting materials with the same classification, which can have deviations in their composition, as indicated by the ranges of values given.

Example #2 (lithium silicate glass ceramic according to the invention)

25

In accordance with the statements made at the start, a lithium silicate material of the following composition in percentage by weight was melted:

SiO_2	56.0 – 59.5
P_2O_5	4.0 – 6.0
Al_2O_3	2.5 – 5.5
Li_2O	13.0 – 15.0
K_2O	1.0 – 2.0
ZrO_2	9.5 – 10.5

CeO ₂	1.0 – 2.0
Tb ₄ O ₇	1.0 – 1.2
Na ₂ O	0.2 – 0.5

The percentage of glass phase was in the range 40 – 60% by volume.

5 The melted material was poured into a mold made from platinum to derive pellets (round rods) and they were then pressed in a dental furnace for pressing ceramics. A press mold with a cavity of rectangular shape was formed using an embedding compound to make specimen rods available so that measurements could be carried out according to Example 1. The dimensions of the rods corresponded to those of test series a) to e). The material was pressed into the press mold at a temperature of 860 °C for 30 minutes. The 25 rods
10 were then removed from the press mold using aluminum oxide particles of mean diameter 110 µm with a jet pressure between 1 and 1.5 bar to reduce the likelihood of damage to a minimum. The edges were then rounded off and the surfaces polished according to the test series a), b) and e) (4th treatment step). No glaze firing was carried out (5th treatment step). Specimens were therefore derived correspondingly, of which half were subjected to
15 flexural strength measurement in accordance with DIN EN ISO 6872:2009-01. The remaining specimens were annealed in an alkali ion melt.

f) Test series #6

20 The edges of ten specimens were rounded off and the surfaces polished. These specimens had a mean flexural strength of 264 MPa. Ten specimens were then annealed in a technically pure KNO₃ salt melt at 420 °C for 10 hours. The mean flexural strength was 464 MPa.

25 g) Test series #7

Ten specimens had a mean flexural strength of 254 MPa. Ten specimens were then annealed in a technically pure KNO₃ salt melt at 500 °C for 10 hours. The mean flexural strength was 494 MPa.

30

h) Test series #8

Ten specimens that had not been annealed had a mean flexural strength of 204 MPa. A further ten specimens were annealed in a technically pure NaNO_3 melt at 480 °C for 10 minutes. The mean flexural strength was 475 MPa.

5

The deviation in the starting strength values is attributable to the different batches and nature of manufacture of the specimens.

Example #3 (glass ceramic of the state of the art)

10

Commercial pellets for pressing in a dental furnace for pressing ceramics were used. According to the data of the manufacturer the pellets had the following composition in percentage by weight:

SiO_2	65.0 – 72.0
P_2O_5	2.5 – 5.0
Al_2O_3	1.5 – 3.5
Li_2O	12.0 – 15.5
K_2O	3.0 – 4.0
ZrO_2	0 – 1.5
CeO_2	0.5 – 2.3
Tb_4O_7	0.5 – 1.0
Na_2O	0 – 0.1

15

The glass phase percentage was in the range 5-15% by volume.

The corresponding pellets were pressed in the dental furnace at 920 °C for 30 minutes. This was followed by the fourth treatment step of rounding off the edges and polishing.

20

i) Test series #9

Measurements involving 10 specimens yielded a mean flexural strength of 422 MPa.

25 Ten specimens were annealed in a technically pure NaNO_3 melt for 20 minutes at 480 °C. The mean flexural strength after annealing was 355 MPa.

Example #4 (glass ceramic according to the state of the art)

Commercially available blocks of lithium silicate ceramic with a composition according to
5 the data of the manufacturer in percentage by weight as follows:

SiO ₂	65.0 – 72.0
P ₂ O ₅	2.5 – 5.0
Al ₂ O ₃	1.5 – 3.5
Li ₂ O	12.0 – 15.5
K ₂ O	3.0 – 4.0
ZrO ₂	0 – 1.5
CeO ₂	0.5 – 2.3
Tb ₄ O ₇	0.5 – 1.0
Na ₂ O	0 – 0.1

Glass phase percentage by volume: 5 – 15 .

10 According to Example 1, to obtain specimen rods with dimensions according to Example I the blocks (form bodies) were grinded, followed by rounding off of the edges and polishing of the surfaces in a third and fourth treatment step.

A final crystallization through heating of the specimens to 850 °C for 10 minutes was
15 carried out to obtain lithium disilicate crystals as the main crystal phase in the specimens.

j) Test series #10

Flexural strength measurements of the aforementioned nature were carried out for ten
20 specimens. A mean value of 352 MPa was found. Ten further specimens were annealed in a technically pure KNO₃ melt for 10 hours at a temperature of 480 °C. The mean flexural strength was 594 MPa.

k) Test series #11

25

Twenty further specimens were prepared from the corresponding batch, wherein the same

treatment steps were carried out, including the final crystallization, but with the exception of the 4th treatment step, so that there was no good mechanical preparation of the specimens (no polishing or rounding off of the edges).

- 5 Ten of the specimens so prepared had a mean flexural strength of 331 MPa. Ten specimens were annealed in a KNO_3 melt at 480 °C for 10 hours. The mean flexural strength was 477 MPa.

1) Test series #12

10

Specimens were prepared as described for test series #10. The ten specimens that were not annealed had a mean flexural strength of 381 MPa. Ten specimens were annealed in a technically pure NaNO_3 melt at 480 °C for 20 minutes. The mean flexural strength was then 348 MPa.

15

A comparison of the examples / test series shows that, at a low total alkali oxide content in the glass phase of the specimens, i.e., after crystallization was carried out, and with a high glass percentage in the ceramic material lithium ions can be replaced by other alkali ions of greater diameter to a sufficient degree, so that the desired surface compressive stress is achieved with the consequence that there is an increase in strength. At the same time an improved chemical resistance was observed. These effects were reduced or not seen at all if the percentage of the glass phase in the form bodies used, i.e., the specimens, was below 20%, in particular below 15%, as is evident from examples 3 and 4. A possible cause – possibly independent of the percentage of the glass phase – is that the alkali oxide content, i.e., the content of sodium oxide and potassium oxide, in the glass phase is more than 2.5% by weight, in particular more than 3% by weight, of the starting composition. The percentage of Li_2O in the starting composition is also likely to have an influence, i.e., a higher percentage of lithium ions enables a greater substitution of sodium oxide and potassium oxide for lithium ions, so that the surface compressive stress is increased.

30

A possible explanation is as follows. The ion exchange that causes the surface compressive stress occurs at the interface between the glass ceramic specimen and the salt melt, wherein the process is controlled through the diffusion of alkali ions of the glass ceramic. Lithium ions diffuse from the glass ceramic to the surface and are replaced by

alkali ions from the salt melt, and alkali ions from the salt melt diffuse after exchange with lithium ions from the surface into the inner part of the glass ceramic. With a high glass phase percentage in the lithium silicate glass ceramic and before annealing relatively low percentage of potassium ions and sodium ions in the glass phase, the motive force and thus the potential for ion exchange is higher / more effective compared to glass ceramic materials in which the glass phase percentage is low and the original alkali ion percentage (sodium oxide and potassium oxide) in the glass phase is relatively high.

This could be additionally intensified through the higher lithium ion percentage in the glass phase, i.e., the lithium ion percentage that is not bound in precipitations and that is therefore available for ion exchange. The precipitations are Li-Si and Li-P precipitations.

Further measurements carried out with lithium silicate glass ceramic specimens revealed that the percentage of the alkali ions replacing the lithium ions starting from the surface extending to a depth of 10 μm is in the range 5 – 20% by weight, at a depth of 8 – 12 μm from the surface the alkali ion percentage is in the range 5 – 10% by weight, at a layer depth between 12 and 14 μm from the surface the percentage of alkali ions is in the range 4 – 8% by weight, at a depth from the surface of between 14 and 18 μm the percentage of alkali ions is in the range 1 – 3% by weight, wherein the percentage by weight of the alkali ions decreases from layer to layer.

Disregarding the deposition of potassium ions compared to the specimens that had not been annealed in a salt melt containing potassium ions, there were no recognizable differences in microstructure, as scanning electron microscope studies showed.

The increase in strength as a result of the creation of surface compressive stress allowed the fabrication of three-unit bridges which had the requisite strength for use in patients. The bridges were fabricated according to the specimens described previously with good mechanical preparation and glaze firing. The preform body was derived from the blank after the first heat treatment step through milling.

Claims

- 5 Method for the production of a form body comprising or containing a lithium silicate glass ceramic as well as form bodies
1. Method for the production of a medical, preferably dental, form body or part thereof comprising or containing a lithium silicate glass ceramic, in particular a bridge,
10 crown, cap, inlay, onlay or veneer,
 w h e r e i n
 in a preform body comprising or containing a lithium silicate glass ceramic with a geometry that corresponds to the form body a surface compressive stress is created by replacement of lithium ions with alkali ions of greater diameter, wherein after
15 substitution of the ions the preform body is used as the form body.
2. Method according to claim 1,
 w h e r e i n
 as alkali ions Na ions, K ions, Cs ions and/or Rb ions are used for creation of the
20 surface compressive stress.
3. Method according to claim 1 or 2,
 w h e r e i n
 the preform body is annealed in a melt containing alkali ions.
25
4. Method according to at least one of the foregoing claims,
 w h e r e i n
 the melt contains one or more elements that impart color to the preform body.
- 30

5. Method according to at least claim 4,
wherein
one or more lanthanides with an atomic number between 58 and 70, preferably cerium, praseodymium, terbium or erbium, is/are used as coloring element or elements.
6. Method according to at least claim 4,
wherein
the at least one color-imparting element is an element of the group vanadium, manganese, iron, yttrium and antimony.
7. Method according to at least claim 4,
wherein
the at least one color-imparting element is dissolved in the melt containing alkali ions.
8. Method according to at least one of the foregoing claims,
wherein
the preform body is annealed in a melt containing potassium ions, in particular a melt containing KNO_3 , KCl or K_2CO_3 , or in a melt containing sodium, in particular in a melt containing NaNO_3 , or in a melt containing a mixture of potassium ions and sodium ions, in particular in a ratio of 50:50 mol%, preferably in a melt containing NaNO_3 and KNO_3 .
9. Method according to at least one of the foregoing claims,
wherein
the preform body is annealed at a temperature T where $T \geq 300\text{ }^\circ\text{C}$, in particular $350\text{ }^\circ\text{C} \leq T \leq 600\text{ }^\circ\text{C}$, preferably $430\text{ }^\circ\text{C} \leq T \leq 530\text{ }^\circ\text{C}$, for a time t , in particular with $t \geq 5$ minutes, preferably $0.5\text{ h} \leq t \leq 10\text{ h}$, especially preferred $3\text{ h} \leq t \leq 8\text{ h}$.

10. Method according to at least one of the foregoing claims,
wherein
the preform body is fabricated from a glass melt, which as starting components
contains at least SiO_2 , Al_2O_3 , Li_2O , K_2O , at least one nucleating agent, such as P_2O_5 ,
and at least one stabilizer such as ZrO_2 .
11. Method according to at least one of the foregoing claims,
wherein
the glass melt contains at least one color-imparting metal oxide, such as CeO_2 and/or
 Tb_4O_7 .
12. Method according to at least one of the foregoing claims,
wherein
the preform body is produced from a glass melt of the following composition in
percentage by weight:
- SiO_2 50 – 80, preferably 52 – 70, especially preferred 56 – 61
 - nucleating agent such as
 P_2O_5 0.5 – 11, preferably 3 – 8, especially preferred 4 – 7
 - Al_2O_3 0 – 10, preferably 0.5 – 5, especially preferred 1.5 – 3.2
 - Li_2O 10 – 25, preferably 13 – 22, especially preferred 14 – 21
 - K_2O 0 – 13, preferably 0.5 – 8, especially preferred 1.0 – 2.5
 - Na_2O 0 – 1, preferably 0 – 0.5, especially preferred 0.2 – 0.5
 - ZrO_2 0 – 20, preferably 4 – 16, in particular 6 – 14, especially
preferred 8 – 12
 - CeO_2 0 – 10, preferably 0.5 – 8, especially preferred 1.0 – 2.5
 - Tb_4O_7 0 – 8, preferably 0.5 – 6, especially preferred 1.0 – 2.0
 - optionally an oxide or a number of oxides of an earth alkali metal or a
number of earth alkali metals of the group magnesium, calcium,
strontium and barium
0 – 20, preferably 0 – 10, especially preferred 0 – 5,
 - optionally an oxide or a number of oxides from the group boron oxide,
tin oxide and zinc oxide

0 – 10, preferably 0 – 7, in particular 0 – 5,

wherein the total sum is 100% by weight.

5 13. Method according to at least one of the foregoing claims

wherein

the glass melt contains as starting components the following constituents in percentage by weight

SiO ₂	58.1 ± 2.0
P ₂ O ₅	5.0 ± 1.5
Al ₂ O ₃	4.0 ± 2.5
Li ₂ O	16.5 ± 4.0
K ₂ O	2.0 ± 0.2
ZrO ₂	10.0 ± 0.5
CeO ₂	0-3, preferably 1.5 ± 0.6
Tb ₄ O ₇	0-3, preferably 1.2 ± 0.4,
Na ₂ O	0 – 0.5, preferably 0.2 – 0.5

10

wherein the total sum is 100% by weight.

14. Method according to at least one of the foregoing claims

wherein

15 a blank is formed from the glass melt during cooling or after cooling to room temperature, with the said blank subjected to at least a first heat treatment W1 at a temperature T_{W1} over a time period t_{W1} , wherein $620\text{ }^{\circ}\text{C} \leq T_{W1} \leq 800\text{ }^{\circ}\text{C}$, in particular $650\text{ }^{\circ}\text{C} \leq T_{W1} \leq 750\text{ }^{\circ}\text{C}$, and/or $1\text{ minute} \leq t_{W1} \leq 200\text{ minutes}$, preferably $10\text{ minutes} \leq t_{W1} \leq 60\text{ minutes}$.

20

15. Method according to at least one of the foregoing claims

wherein

the first heat treatment W1 is carried out in two stages, wherein in particular in the first stage a temperature T_{S11} of $630\text{ }^{\circ}\text{C} \leq T_{S11} \leq 690\text{ }^{\circ}\text{C}$ and/or in the second stage a temperature T_{S12} of $720\text{ }^{\circ}\text{C} \leq T_{S12} \leq 780\text{ }^{\circ}\text{C}$ is set and/or the heat-up rate A_{S11} up to the temperature T_{S11} is $1.5\text{ K/min} \leq A_{S11} \leq 2.5\text{ K/min}$ and/or the heat-up rate A_{S12} up to the temperature T_{S12} is $8\text{ K/min} \leq A_{S12} \leq 12\text{ K/min}$.

16. Method according to at least one of the foregoing claims

wherein

following the first heat treatment W1 the lithium silicate glass ceramic blank is subjected to a second heat treatment W2 at a temperature T_{W2} over a time period t_{W2} wherein $800\text{ }^{\circ}\text{C} \leq T_{W2} \leq 1040\text{ }^{\circ}\text{C}$, preferably $800\text{ }^{\circ}\text{C} \leq T_{W2} \leq 870\text{ }^{\circ}\text{C}$, and/or $2\text{ minutes} \leq t_{W2} \leq 200\text{ minutes}$, preferably $3\text{ minutes} \leq t_{W2} \leq 30\text{ minutes}$.

17. Method according to at least one of the foregoing claims

wherein

after one of the heat treatment steps, in particular after the first heat treatment step, the preform body is derived from the blank through grinding and/or milling.

18. Form body in the form of a medical, in particular dental, object or part thereof, in particular a bridge, crown, cap, inlay, onlay, veneer comprising or containing a lithium silicate glass ceramic

wherein

a surface compressive stress is created in the form body by replacement of lithium ions with alkali ions of greater diameter.

19. Form body according to claim 18,

wherein,

the alkali ions are Na ions, K ions, Cs ions and/or Rb ions, in particular Na ions or K ions, or Na ions and K ions.

20. Form body according to claim 18 or claim 19,
wherein
in a glass phase of the form body at least one stabilizer that increases the rigidity of
the form body, especially in the form of ZrO_2 , is present with a percentage by weight
5 in the initial composition of the form body that is preferably 8 – 12 wt.%.
21. Form body according to at least one of the claims 18 - 20,
wherein
the form body is produced from a glass melt that is of the following composition
10 in percentage by weight
- SiO_2 50 – 80, preferably 52 – 70, especially preferred 56 – 61
 - nucleating agent such as
 P_2O_5 0.5 – 11, preferably 3 – 8, especially preferred 4 – 7
 - Al_2O_3 0 – 10, preferably 0.5 – 5, especially preferred 1.5 – 3.2
 - 15 - Li_2O 10 – 25, preferably 13 – 22, especially preferred 14 – 21
 - K_2O 0 – 13, preferably 0.5 – 8, especially preferred 1.0 – 2.5
 - Na_2O 0 – 1, preferably 0 – 0.5, especially preferred 0.2 – 0.5
 - ZrO_2 0 – 20, preferably 4 – 16, in particular 6 – 14, especially
preferred 8 – 12
 - 20 - CeO_2 0 – 10, preferably 0.5 – 8, especially preferred 1.0 – 2.5
 - Tb_4O_7 0 – 8, preferably 0.5 – 6, especially preferred 1.0 – 2.0
 - optionally an oxide or a number of oxides of an earth alkali metal or a
number of earth alkali metals from the group magnesium, calcium,
strontium, barium
25 0 – 20, preferably 0 – 10, especially preferred 0 – 5 ,
 - optionally an oxide or a number of oxides from the group boron oxide,
tin oxide, zinc oxide
0 – 10, preferably 0 – 7, in particular 0 – 5 ,
- wherein the total sum is 100% by weight.

22. Form body according to at least one of the claims 18 -21,
wherein
the form body is produced from a glass melt that has the following composition in
percentage by weight:

5

SiO ₂	58.1 ± 2.0
P ₂ O ₅	5.0 ± 1.5
Al ₂ O ₃	4.0 ± 2.5
Li ₂ O	16.5 ± 4.0
K ₂ O	2.0 ± 0.2
ZrO ₂	10.0 ± 0.5
CeO ₂	0 - 3, preferably 1.5 ± 0.6
Tb ₄ O ₇	0 - 3, preferably 1.2 ± 0.4,
Na ₂ O	0 – 0.5, preferably 0.2 – 0.5

with a total sum of 100% by weight.

23. Form body according to at least one of the claims 18 - 22,
wherein
the form body contains a glass phase is in the range 20 – 65% by volume.

10

24. Form body according to at least one of the claims 18 - 23,
wherein
35 – 80% by volume of the form body are lithium silicate crystals.

15

25. Form body according to at least one of the claims 18 to 24,
wherein
the percentage of the alkali ions replacing the lithium ions starting from the surface
extending to a depth of 10 µm is in the range 5 – 20% by weight, and/or at a depth of
8 – 12 µm from the surface the alkali ion percentage is in the range 5 – 10% by
weight, and/or at a layer depth between 12 and 14 µm from the surface the
percentage of alkali ions is in the range 4 – 8% by weight, and/or at a depth from the
surface of between 14 and 18 µm the percentage of alkali ions is in the range 1 – 3%

20

by weight, wherein the percentage by weight of the alkali ions decreases from layer to layer.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/051881

A. CLASSIFICATION OF SUBJECT MATTER INV. C03C3/097 C03C4/00 C03C4/02 C03C4/20 C03C10/00 C03C21/00 A61C13/083 ADD. According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C03C A61C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	DE 20 2011 110343 U1 (IVOCLAR VIVADENT AG [LI]) 16 July 2013 (2013-07-16) the whole document especially examples and tables I to IV and claims 1-24 -----	1-25
Y	WO 2012/175615 A1 (FRAUNHOFER GES ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E V [DE]; RAU) 27 December 2012 (2012-12-27) the whole document especially examples, tables 1-3 and claims 1-17 ----- -/-	1-25
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 22 March 2016		Date of mailing of the international search report 01/04/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Heer, Stephan

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Information on patent family members

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