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**(54) Title:** METHOD FOR PRODUCING A LITHIUM SILICATE GLASS PREFORM AND A LITHIUM SILICATE GLASS CERAMIC PREFORM

**(54) Bezeichnung :** VERFAHREN ZUR HERSTELLUNG EINES LITHIUMSILIKAT-GLASROHLLINGS UND EINES LITHIUMSILIKAT-GLASKERAMIKROHLLINGS

**WO 2015/144866 A1**

**(57) Abstract:** The invention relates to a method for producing a lithium silicate glass preform having an initial composition containing at least 8% by weight of a stabilizer from the group of  $ZrO_2$ ,  $HfO_2$  and mixtures thereof, comprising the steps of - mixing of raw materials containing the stabilizer in powder form, the particle size of the powder being  $d_{50} = x$ , where  $0.3 \mu m \leq x \leq 1.5 \mu m$ , - melting the raw materials in a container at a temperature  $T_{AU}$  and retaining the melt in the container for a time  $t_H$ , - drawing the homogenized melt off into vessels, the outflow temperature  $T_{AB}$  of the melt exiting the container being  $T_{AU} \geq T_{AB}$ , and the filling of the vessels and the shaping of the melt therein taking place at a cooling rate A.

**(57) Zusammenfassung:** Die Erfindung bezieht sich auf ein Verfahren zur Herstellung eines Lithiumsilikat Glasrohlings mit einer Anfangszusammensetzung mit zumindest 8 Gew.-% eines Stabilisators aus der Gruppe  $ZrO_2$ ,  $HfO_2$  oder Mischungen dieser, umfassend die Verfahrensschritte - Mischen von den Stabilisatoren in Pulverform enthaltenden Rohstoffen, wobei das Pulver eine Korngröße  $d_{50} = x$  mit  $0,3 \mu m \leq x \leq 1,5 \mu m$  aufweist, - Aufschmelzen der Rohstoffe bei einer Temperatur  $T_{AU}$  in einem Behälter und Halten der Schmelze in dem Behälter über eine Zeit  $t_H$ , - Abfüllen der homogenisierten Schmelze in Behältnisse, wobei die Abflusstemperatur  $T_{AB}$  aus dem Behälter beträgt  $T_{AU} \geq T_{AB}$ , wobei das Befüllen der Behältnisse und Formgeben der Schmelze in diesen mit einer Abkühlrate A erfolgt.

## Description

### Method for producing a lithium silicate glass blank and a lithium silicate glass-ceramic blank

The invention relates to a method for producing a lithium silicate glass blank with a composition of at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $ZrO_2$ ,  $HfO_2$ , or mixtures thereof. The invention also relates to a method for producing a lithium silicate glass-ceramic blank, and the use of the lithium silicate glass-ceramic blank. The invention also relates to the use of the lithium silicate glass-ceramic blank as well as to a dental product.

Lithium silicate glass-ceramic blanks have been proven their value in the field of dental prosthetics due to their strength and biocompatibility. There is the advantage that, if a lithium silicate blank comprises lithium metasilicate as main crystalline phase, an easy machining is possible without undue wear of tools. If then a heat treatment takes place, during which the product is converted into a lithium disilicate glass-ceramic, a high strength is obtained. Also good optical properties and a good chemical stability are given. Respective methods are disclosed in DE 197 50 794 A1, or DE 103 36 913 B4.

It has been shown that the strength is increased and a good translucence can be reached, if at least a stabilizer selected from the group zirconium oxide, hafnium oxide, or mixtures thereof, especially zirconium oxide, is added to the starting raw materials in form of lithium carbonate, quartz, aluminum oxide, etc., which are usual initial components. The percentage by weight of the stabilizer in the initial composition can be as high as 20 %. In this respect, reference is made to DE 10 2009 060 274 A1, or WO 2012/175450 A1, WO 2012/175615 A1, WO 2013/053865 A2, or EP 2 662 342 A1.

In practice, however, problems arise in such a way that after the final crystallization, i.e., especially at the stage when lithium disilicate is existent as main crystalline phase in the lithium silicate glass, the stabilizers, especially zirconium oxide, recrystallize although the latter had been fully dissolved in the glass phase of the lithium silicate before.

One of the objects of the invention is to provide a method for producing a lithium silicate glass blank making sure that the stabilizer does not recrystallize during any subsequent heat treatment, in particular when lithium disilicate exists as main crystalline phase.

Another object is to make sure that the melt to be poured can be shaped on an industrial scale and in a reproducible manner to dental products, such as pressed pellets, or be molded to blocks to be machined by CAD/CAM-processes. When filling the molds, a so called “sloshing” of the melt within the molds shall be prevented as to avoid that the desired smooth, horizontally extending surface of the solidified blanks could not be obtained.

To solve at least one of the above-mentioned problems, the invention provides a method for producing a lithium silicate glass blank with at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $ZrO_2$ ,  $HfO_2$ , or mixtures thereof comprising the method steps:

- mixing the raw materials comprising the stabilizer in powder form, wherein the powder of the stabilizer has a particle size  $d_{50} = x$  with  $0.3 \mu m \leq x \leq 1.5 \mu m$ ,
- melting the raw materials in a crucible at a temperature  $T_{AU}$  and storing the melt in the crucible for a time  $t_H$ ,
- pouring the homogenized melt into molds, wherein the melt flows out of the crucible with a discharge temperature  $T_{AB}$  being  $T_{AU} \geq T_{AB}$ , wherein the filling of the molds and the molding of the melt in the molds takes place with a cooling rate A.

The invention is also characterized by a method for producing a lithium silicate glass blank with a composition of at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $ZrO_2$ ,  $HfO_2$ , or mixtures thereof, with the method steps:

- mixing the raw materials comprising the stabilizer in powder form, wherein the powder of the stabilizer has a particle size  $d_{50} = x$  with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ ,
- melting the raw materials in a crucible at a temperature  $T_{AU}$  and storing the melt in the crucible for a time  $t_H$ ,
- pouring the homogenized melt into molds, wherein the melt flows out of the crucible with a discharge temperature  $T_{AB}$  being  $T_{AU} - Y \text{ } ^\circ\text{C} = T_{AB}$  with  $150 \text{ } ^\circ\text{C} \leq Y \leq 350 \text{ } ^\circ\text{C}$  and  $T_{AU} \geq 1400 \text{ } ^\circ\text{C}$ , wherein the filling of the molds and the molding of the melt in the molds takes place with a cooling rate A.

According to the invention, a method for producing a lithium silicate glass blank with a composition of at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $ZrO_2$ ,  $HfO_2$ , or mixtures thereof, comprises the method steps:

- mixing the raw materials comprising the stabilizer in powder form, wherein the powder of the stabilizer has a particle size  $d_{50} = x$  with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ ,
- melting the raw materials in a crucible at a temperature  $T_{AU}$  and storing the melt in the crucible for a time  $t_H$ ,
- pouring the homogenized melt into molds, wherein the melt flows out of the crucible with a discharge temperature  $T_{AB}$  being  $T_{AU} \geq T_{AB}$ , wherein the filling of the molds and the molding of the melt in the molds takes place with a cooling rate A with  $5 \text{ K/sec} \leq A \leq 100 \text{ K/sec}$  up to a temperature  $T_M$  with  $T_M \geq 600 \text{ } ^\circ\text{C}$ , particularly  $600 \text{ } ^\circ\text{C} \leq T_M \leq 650 \text{ } ^\circ\text{C}$ .

The invention also relates to a method for producing a lithium silicate glass blank with a composition of at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $ZrO_2$ ,  $HfO_2$ , or mixtures thereof, wherein the method comprises the steps:

- mixing the raw materials comprising the stabilizer in powder form, wherein the powder of the stabilizer has a particle size  $d_{50} = x$  with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ ,
- melting the raw materials in a crucible at a temperature  $T_{AU}$  with  $1450 \text{ }^\circ\text{C} \leq T_{AU} \leq 1600 \text{ }^\circ\text{C}$  and storing the melt in the crucible for a time  $t_H$  with  $t_H \geq 1 \text{ h}$ ,
- pouring the homogenized melt into molds, wherein the melt flows out of the crucible with a discharge temperature  $T_{AB}$  being  $T_{AU} \geq T_{AB}$ , wherein the filling of the molds and the molding of the melt in the molds takes place with a cooling rate A.

The invention relates in particular to a method for producing a lithium silicate glass blank with a composition with at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $ZrO_2$ ,  $HfO_2$ , or mixtures thereof, comprising the method steps

- mixing the raw materials comprising the stabilizer in powder form, wherein the powder of the stabilizer has a particle size  $d_{50} = x$  with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ ,
- melting the raw materials in a crucible at a temperature  $T_{AU}$  with  $1450 \text{ }^\circ\text{C} \leq T_{AU} \leq 1600 \text{ }^\circ\text{C}$  and storing the melt in the crucible for a time  $t_H$  with  $t_H \geq 1 \text{ h}$ ,
- pouring the homogenized melt into molds, wherein the melt flows out of the crucible with a discharge temperature  $T_{AB}$  being  $T_{AU} - Y \text{ }^\circ\text{C} = T_{AB}$  with  $150 \text{ }^\circ\text{C} \leq Y \leq 350 \text{ }^\circ\text{C}$  and  $T_{AU} \geq 1400 \text{ }^\circ\text{C}$ , wherein the filling of the molds and the molding of the melt in the molds takes place with a

cooling rate A with  $5 \text{ K/sec} \leq A \leq 100 \text{ K/sec}$  up to a temperature  $T_M$  with  $600 \text{ }^\circ\text{C} \leq T_M$ , particularly  $600 \text{ }^\circ\text{C} \leq T_M \leq 650 \text{ }^\circ\text{C}$ .

It has surprisingly been shown that, when the stabilizer in powder form, especially zirconium oxide powder, has a particle size  $d_{50}$  between  $0.3 \text{ } \mu\text{m}$  and  $1.5 \text{ } \mu\text{m}$ , the zirconium oxide dissolves well and remains in solution, namely is existent in an amorphous phase, i.e., the glass, even when the melt is poured into the crucible, cooled and then being subjected to one or several heat treatments to form at least lithium disilicate crystals. At the same time, there is the advantage that problems with agglomeration do not occur.

The terms  $d_{50}$ ,  $d_{10}$ ,  $d_{90}$  mean that 50%, and 10%, and 90%, respectively, of the particles have a particle size that is smaller than the given value for the particle size.

To avoid “sloshing,” it has been proven advantageous when the glass melt flows out of the crucible with a discharge temperature  $T_{AB} 1200 \text{ }^\circ\text{C} \leq T_{AB} \leq 1350 \text{ }^\circ\text{C}$ , preferably  $1250 \text{ }^\circ\text{C} \leq T_{AB} \leq 1300 \text{ }^\circ\text{C}$ . When the melt is filled into the molds, the melt should have a temperature  $T_B$  not less than  $T_B = 1150 \text{ }^\circ\text{C}$  without any disadvantages being observed as to the finished shape of the lithium silicate glass blanks after the melt has cooled in the crucible.

Cooling the melt relative to the temperature, at which the raw materials are melted and homogenized by convection, without using mechanical auxiliary means such as a stirrer, provides the advantage that the melt has a viscosity which makes it possible to fill the molds in a reproducible manner and to obtain a horizontally extending surface at the same time. Possibly, the prevention of recrystallization is also supported by the melt in the crucible cooling with a cooling rate in a range between  $5 \text{ K/sec}$  and  $100 \text{ K/sec}$  which prevents the forming of nuclei for the stabilizer material. The cooling rate is applicable at least up to a temperature  $T_M \geq 600 \text{ }^\circ\text{C}$ , especially  $600 \text{ }^\circ\text{C} \leq T_M \leq 650 \text{ }^\circ\text{C}$ .

Subsequently, a cooling to room temperature can take place in the usual fashion.

The homogenizing of the melt is also important, wherein it has proved advantageous, to keep the melt at a temperature  $T_{AU}$  which is between 1500 °C and the high temperature strength of the used crucible material, such as platinum alloy, for a time of at least 1 hour, especially for a time period between 2 and 7 hours. A multiple melting is not necessary.

Thus, the invention is also characterized in that after melting and homogenizing the raw materials in the crucible, especially by convection, the melt is poured into the molds immediately.

Consequently, the invention is characterized and differs from the prior art preferably in that it is not necessary to produce and remelt a frit without causing disadvantages with regard to the homogenization. Thus, in the light of the prior art, the invention provides in general a shorter duration of process and/or a more cost-effective production of the blank.

Of course, it is still within the scope of the invention to remelt a produced frit.

It is also possible to cool the melt which is homogenized in the crucible by convection during the homogenization process. In doing so, the melt can be kept, for instance, for a first period of time of 2 to 6 hours at a temperature  $T_1$  with  $1450 \text{ } ^\circ\text{C} \leq T_1 \leq 1550 \text{ } ^\circ\text{C}$ , and then kept for a second period of time at a temperature  $1200 \text{ } ^\circ\text{C} \leq t_2 \leq 1300 \text{ } ^\circ\text{C}$  for a time  $t_2$ , to be subsequently poured to fill the molds.

The invention is particularly characterized in that the used powder further has a particle size  $d_{10} = 0.5 \cdot x$  and/or  $d_{90} = 1.5 \cdot x$ , especially  $d_{10} = 0.5 \cdot x$  and  $d_{90} = 1.5 \cdot x$ , with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ .

These secondary conditions ensure that the content of small particles is so low that agglomeration does not occur. Limiting the number of large particles also ensures sufficient dissolution of the stabilizer.

It is specifically provided that the stabilizer comprises more than 90 wt-%  $\text{ZrO}_2$ , especially more than 95 wt-%  $\text{ZrO}_2$ , preferably more than 97.5 wt-%  $\text{ZrO}_2$ .

Preferably, the composition of the blank comprises the following components (data in % by weight):

$\text{SiO}_2$	46.0 – 72.0
$\text{Li}_2\text{O}$	10.0 – 25.0
$\text{ZrO}_2$	8.0 – 20.0
$\text{Al}_2\text{O}_3$	0.1 – 8.0
$\text{K}_2\text{O}$	0.1 – 5.0
$\text{CeO}_2$	0.0 – 4.0
$\text{B}_2\text{O}_3$	0.0 – 4.0
$\text{Na}_2\text{O}$	0.0 – 4.0
$\text{Tb}_4\text{O}_7$	0.0 – 2.5

at least one nucleating agent 1.0 – 10.0,  
such as  $\text{P}_2\text{O}_5$ ,  
and 0.0 to 4.0 of at least one additive,

wherein the total sum is 100 wt-%.

The additive can be at least one oxide selected from the group  $\text{BaO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{SM}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Y}_2\text{O}_3$ .

Further, the invention is characterized by a method for producing a lithium silicate glass-ceramic blank by using the lithium silicate glass blank, according to one or more of the aforementioned method steps, wherein the cooled melt which was poured into

molds is subjected to at least a first heat treatment W1 at a temperature  $T_{W1}$  for a period of time  $t_{W1}$ , with  $620 \text{ }^{\circ}\text{C} \leq T_{W1} \leq 800 \text{ }^{\circ}\text{C}$ , especially  $650 \text{ }^{\circ}\text{C} \leq T_{W1} \leq 750 \text{ }^{\circ}\text{C}$ , and/or  $1 \text{ min} \leq t_{W1} \leq 200 \text{ min}$ , preferably  $10 \text{ min} \leq t_{W1} \leq 60 \text{ min}$ .

By carrying out this step, nucleating agents and lithium metasilicate crystals are formed.

Such a lithium silicate glass-ceramic blank can easily be machined with a minimal wear of tools. Such a blank can also be pressed to a desired geometry.

Particularly to achieve a final crystallization, especially to form lithium disilicate crystals and/or to convert the metasilicate crystals into disilicate crystals, it is provided that the lithium silicate glass-ceramic blank is subjected after the first heat treatment W1 to a second heat treatment W2 at a temperature  $T_{W2}$  for a time  $t_{W2}$ , with  $800 \text{ }^{\circ}\text{C} \leq T_{W2} \leq 1040 \text{ }^{\circ}\text{C}$ , preferably  $800 \text{ }^{\circ}\text{C} \leq T_{W2} \leq 900 \text{ }^{\circ}\text{C}$ , and/or  $5 \text{ min} \leq t_{W2} \leq 200 \text{ min}$ , preferably  $5 \text{ min} \leq t_{W2} \leq 30 \text{ min}$ .

For the heat treatment steps leading to nucleation and precrystallization and final crystallization respectively, preferably the following temperature values and heating rates are chosen. Regarding the first heat treatment, it is specifically provided for it to be carried out in two steps, wherein at a first step, the temperature is held between  $640 \text{ }^{\circ}\text{C}$  and  $680 \text{ }^{\circ}\text{C}$ , and at a second holding step between  $720 \text{ }^{\circ}\text{C}$  and  $780 \text{ }^{\circ}\text{C}$ . The heated blank is kept at every step for a period of time, wherein at the first step the period of time preferably is between 35 and 45 minutes, and at the second step between 15 and 25 minutes.

Such lithium silicate glass-ceramic blanks show a high translucence and chemical stability. They are characterized by their strength. A precipitation of stabilizer material, especially zirconium oxide, cannot be found. Thus, said lithium silicate glass blanks are

especially suitable for dental materials or as components of dental materials, wherein possible applications include shaped dental products in the form of, for instance, inlays, onlays, bridges, veneers, facets, crowns, partial crowns, abutments.

In particular, lithium silicate glass-ceramic blanks are extremely easy to machine by CAD/CAM, wherein after the further heat treatment a highly transparent and high-strength product is provided which has a high chemical stability.

Further details, advantages and features of the invention derive not only from the claims and their features, *per se* and/or in combination, but also from the following examples.

Raw materials, such as lithium carbonate, quartz, aluminum oxide, zirconium oxide were mixed on an industrial scale by means of a tumble mixer until a visually homogeneous mixture existed. In doing so, a total of 5 mixtures were produced, differing from each other in the particle size of the zirconium oxide.

The composition of the test pieces for the conducted tests was the following (data in % by weight):

SiO <sub>2</sub>	58 – 60
Li <sub>2</sub> O	13.5 – 20.5
ZrO <sub>2</sub>	9.0 – 12.5
P <sub>2</sub> O <sub>5</sub>	3.0 – 7.5
Al <sub>2</sub> O <sub>3</sub>	0.5 – 6.0
K <sub>2</sub> O	0.5 – 3.5
CeO <sub>2</sub>	0.5 – 2.5
B <sub>2</sub> O <sub>3</sub>	0 – 3
Na <sub>2</sub> O	0 – 3
Tb <sub>4</sub> O <sub>7</sub>	0 – 1.5

Example 1:

A zirconium oxide powder with a particle size  $d_{50}$  = approximately 15  $\mu\text{m}$ ,  $d_{10}$  = 10.8  $\mu\text{m}$ ,  $d_{90}$  = 34.9  $\mu\text{m}$  was used.

The mixture was melted in a high temperature resistant crucible made of platinum alloy at 1450 °C for a time of 2.25 hours. Then, the melt was cooled in the crucible, at first kept at 1450 °C for half an hour, and then kept at 1250 °C for half an hour. Subsequently, the melt was poured into molds suitable for pressed pellets or blocks to be machined. The pellets and blocks respectively should have a volume of 1  $\text{cm}^3$  to 2  $\text{cm}^3$ . The cooling rate was 70 K/sec up to 600 °C, then, a cooling down to room temperature took place. An amorphous and, thus, translucent glass was obtained. Then, the blanks were subjected to a crystallization firing, wherein during the first heat treatment the blanks were kept at 660 °C for 60 minutes, and then, during a second heat treatment, kept at 850 °C for 8 minutes. Then a cooling down to room temperature took place. During an inspection of the glass-ceramic, single zirconium oxide precipitations were found which made the glass-ceramic opaque.

Example 2:

Zirconium oxide powder with a particle size  $d_{50}$  = approximately 0.7  $\mu\text{m}$ ,  $d_{10}$  = 0.2  $\mu\text{m}$ ,  $d_{90}$  = 2.2  $\mu\text{m}$  was used.

The mixture was melted in a high temperature resistant crucible made of platinum alloy at a temperature  $T = 1500$  °C and kept at this temperature for 6 hours. Subsequently, the melt was poured into molds suitable for pressed pellets or blocks to be machined. The pellets and blocks respectively should have a volume of 1  $\text{cm}^3$  to 2  $\text{cm}^3$ . The cooling rate was 70 K/sec up to 600 °C. Then, a cooling down to room temperature took place. An amorphous and, thus, translucent glass was obtained. Then, the blanks were

subjected to a crystallization firing. For nucleation and/or precrystallization the glass was at first heated with a heating rate of 2 K/min from room temperature to 660 °C, and kept at this temperature for 40 minutes. Then a further heating took place to 750 °C with a heating rate of 10 K/min. This temperature was kept for 20 minutes. The final crystallization followed subsequently at a temperature of 850 °C for 8 minutes. Then a cooling down to room temperature took place. During an inspection of the glass-ceramic no zirconium oxide precipitations were found.

Example 3:

A zirconium oxide powder with a particle size  $d_{50}$  = approximately 0.7  $\mu\text{m}$ ,  $d_{10}$  = 0.2  $\mu\text{m}$ ,  $d_{90}$  = 2.2  $\mu\text{m}$  was used.

The mixture was melted in a high temperature resistant crucible made of platinum alloy at 1500 °C for a time of 6 hours. The melt was then cooled in the crucible and kept at 1250 °C for half an hour. Subsequently, the melt was poured into molds suitable for pressed pellets or blocks to be machined. The pellets and blocks respectively should have a volume of 1  $\text{cm}^3$  to 2  $\text{cm}^3$ . The cooling rate was 70 K/sec up to 600 °C. Then, a cooling down to room temperature took place. An amorphous and, thus, translucent glass was obtained. Then the blanks were subjected to a crystallization fire. For nucleation and/or precrystallization the glass was at first heated from room temperature to 660 °C with a heating rate of 2 K/min, and kept at this temperature for 40 minutes. Subsequently, a further heating to 750 °C with a heating rate of 10 K/min took place. This temperature was kept for 20 minutes. Subsequently, the final crystallization took place at a temperature of 850 °C for 8 minutes. Then a cooling down to room temperature took place. During an inspection of the glass-ceramic, no zirconium oxide precipitations were found.

Example 4:

A zirconium oxide powder with a particle size  $d_{50}$  = approximately 0.7  $\mu\text{m}$ ,  $d_{10}$  = 0.2  $\mu\text{m}$ ,  $d_{90}$  = 2.2  $\mu\text{m}$  was used.

The mixture was melted in a high temperature resistant crucible made of platinum alloy at 1500 °C for a time of 6 hours. The melt was then cooled and kept in the crucible at 1200 °C for half an hour. Subsequently, the melt was poured into molds suitable for pressed pellets or blocks to be machined. The pellets and blocks respectively should have a volume of 1  $\text{cm}^3$  to 2  $\text{cm}^3$ . The cooling rate was 70 K/sec down to 600 °C. Then a cooling down to room temperature took place. An amorphous and, thus, translucent glass was obtained. Then the blanks were subjected to a crystallization fire. In doing so, the glass was at first heated from room temperature to 660 °C with a heating rate of 2 K/min, and kept at this temperature for 40 minutes. Subsequently, a further heating to 750 °C with a heating rate of 10 K/min took place. This temperature was kept for 20 minutes. Subsequently, the final crystallization took place at a temperature of 850 °C for 8 minutes. Then a cooling down to room temperature took place. During an inspection of the glass-ceramic single zirconium oxide precipitations were found that made the glass-ceramic opaque.

Example 5:

A zirconium oxide powder with a particle size  $d_{50}$  = approximately 5  $\mu\text{m}$ ,  $d_{10}$  = 0.3  $\mu\text{m}$ ,  $d_{90}$  = 5.8  $\mu\text{m}$  was used.

The mixture was melted in a high temperature resistant crucible made of platinum alloy at 1500 °C for a time of 4 hours. The melt was then cooled in the crucible and kept at 1450 °C for one hour. Subsequently, the melt was poured into molds suitable for pressed pellets or blocks to be machined. The pellets and blocks should have a volume of 1  $\text{cm}^3$  to 2  $\text{cm}^3$ . The cooling rate was 70 K/sec up to 600 °C. Then, a cooling down to room temperature took place. An amorphous and, thus, translucent glass was obtained.

Then the blanks were subjected to a crystallization firing, wherein the blanks were kept at 620 °C for 60 minutes (precrystallization), and then, during a second heat treatment, kept at 850 °C for 8 minutes (final crystallization). Then a cooling to room temperature took place. During an inspection of the glass-ceramic, numerous small precipitations of zirconium oxide were found that made the glass-ceramic opaque.

It follows from the aforementioned examples that by using zirconium oxide powder with a particle size of  $d_{50} = 0.7 \mu\text{m}$ , a melting temperature of 1500 °C and a discharge temperature that is lower than the melting temperature, glass-ceramic bodies can be produced in which zirconium precipitations cannot be found. The glass-ceramic bodies had a high translucence. Chemical and mechanical tests showed a high durability and strength.

The claims defining the invention are as follows:

1. A method for producing a lithium silicate glass blank with a composition of at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group  $\text{ZrO}_2$ ,  $\text{HfO}_2$ , or mixtures thereof, comprising the method steps:
  - mixing the raw materials containing the stabilizer in powder form, wherein the powder has a particle size  $d_{50} = x$  with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ ,
  - melting the raw materials in a crucible at a temperature  $T_{AU}$ , with  $1450^\circ\text{C} \leq T_{AU} \leq 1600^\circ\text{C}$ , and keeping the melt in the crucible for a time  $t_H$ , with  $t_H \geq 1\text{h}$ ,
  - pouring the homogenized melt into molds, whereby the discharge temperature  $T_{AB}$  of the melt out of the crucible follows  $T_{AU} - Y^\circ\text{C} = T_{AB}$ , with  $150^\circ\text{C} \leq Y \leq 350^\circ\text{C}$ , whereby the filling of the molds and the molding of the melt in the molds takes place with a cooling rate  $A$ , with  $5 \text{ K/sec} \leq A \leq 100 \text{ K/sec}$ , to a temperature  $T_M$ , with  $600^\circ\text{C} \leq T_M$ , in particular  $600^\circ\text{C} \leq T_M \leq 650^\circ\text{C}$ .
2. The method of claim 1, wherein the employed powder has a particle size  $d_{10} = 0.5 \cdot x$  and/or  $d_{90} = 1.5 \cdot x$ , in particular  $d_{10} = 0.5 \cdot x$  and  $d_{90} = 1.5 \cdot x$ , with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ .
3. The method of claim 1 or claim 2, wherein during the filling of the molds, the melt is at a temperature  $T_B$ , with  $1150^\circ\text{C} \leq T_B < T_{AB}$ .
4. The method of claim 1, wherein the raw materials, or the melt created from the raw materials, is maintained at the temperature  $T_{AU}$  in the crucible for a time  $t_H$ , with  $2 \text{ h} \leq t_H \leq 7 \text{ h}$ .
5. The method of any one of the preceding claims wherein the melt in the crucible is homogenized by convective flow, wherein, if necessary, the melt is cooled in the crucible during the homogenization.

6. The method of any one of the preceding claims, wherein the melt is cooled in the discharge region of the crucible to a temperature  $T_{AB}$ , especially with  $1200\text{ }^{\circ}\text{C} \leq T_{AB} \leq 1300\text{ }^{\circ}\text{C}$ .
7. The method of any one of the preceding claims, wherein the stabilizer contains more than 90 wt-%  $\text{ZrO}_2$ , in particular more than 95 wt-%  $\text{ZrO}_2$ , preferably more than 97.5 wt-%  $\text{ZrO}_2$ .
8. The method of any one of the preceding claims, wherein after melting and homogenizing the raw materials in the crucible, in particular by convective flow, the melt is poured directly into the molds.
9. The method of any one of the preceding claims, wherein the blank has a composition of (in % by weight):

$\text{SiO}_2$	46.0 – 72.0
$\text{Li}_2\text{O}$	10.0 – 25.0
$\text{ZrO}_2$	8.0 – 20.0
$\text{Al}_2\text{O}_3$	0.1 – 8.0
$\text{K}_2\text{O}$	0.1 – 5.0
$\text{CeO}_2$	0.0 – 4.0
$\text{B}_2\text{O}_3$	0.0 – 4.0
$\text{Na}_2\text{O}$	0.0 – 4.0
$\text{Tb}_4\text{O}_7$	0.0 – 2.5

at least one nucleating agent 1.0 – 10.0, such as  $\text{P}_2\text{O}_5$ , as well as 0.0 to 4.0 of at least one additive,

whereby the additive is at least one oxide selected from the group  $\text{BaO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Y}_2\text{O}_3$ , and the sum total is 100 wt-%.

10. The method of any one of the preceding claims, wherein the blank has a composition of (in % by weight):

$\text{SiO}_2$	58 – 60
$\text{Li}_2\text{O}$	13.5 – 20.5

ZrO <sub>2</sub>	9.0 – 12.5
nucleating agent, particularly P <sub>2</sub> O <sub>5</sub> ,	3.0 – 7.5
Al <sub>2</sub> O <sub>3</sub>	0.5 – 6.0
K <sub>2</sub> O	0.5 – 3.5
CeO <sub>2</sub>	0.5 – 2.5
B <sub>2</sub> O <sub>3</sub>	0 – 3
Na <sub>2</sub> O	0 – 3
Tb <sub>4</sub> O <sub>7</sub>	0 – 1.5,

whereby the sum total is 100 wt-%.

11. A method for producing a lithium silicate glass-ceramic blank, comprising the method steps:  
producing a lithium silicate glass blank with a composition of at least 8 wt-%, preferably 9 to 20 wt-%, of a stabilizer selected from the group ZrO<sub>2</sub>, HfO<sub>2</sub>, or mixtures thereof, comprising the method steps
  - mixing the raw materials containing the stabilizer in powder form, wherein the powder has a particle size  $d_{50} = x$  with  $0.3 \mu\text{m} \leq x \leq 1.5 \mu\text{m}$ ,
  - melting the raw materials in a crucible at a temperature  $T_{AU}$  and storing the melt in the crucible for a time  $t_H$ ,
  - pouring the homogenized melt into molds, wherein the discharge temperature out of the melt is  $T_{AB}$ , with  $T_{AU} \geq T_{AB}$ , wherein the filling of the molds and the molding of the melt in the molds takes place with a cooling rate A,subjecting the melt, after having been filled into the molds and cooled in the molds, to at least one thermal treatment W1 at a temperature  $T_{W1}$  for a duration  $t_{W1}$ , whereby  $620^\circ\text{C} \leq T_{W1} \leq 800^\circ\text{C}$ , and/or  $1 \text{ min} \leq t_{W1} \leq 200 \text{ min}$ .
12. The method of claim 11, wherein the first heat treatment W1 is carried out in two stages, whereby one in particular uses a temperature  $T_{St1}$  in the first stage, with  $630^\circ\text{C} \leq T_{St1} \leq 690^\circ\text{C}$ , and/or a temperature  $T_{St2}$  in the second stage, with  $720^\circ\text{C} \leq T_{St2} \leq 780^\circ\text{C}$ .

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13. The method of claim 11 or claim 12, wherein after the first thermal treatment W1, the lithium silicate glass-ceramic blank is subjected to a second thermal treatment W2 at a temperature  $T_{W2}$  for a time  $t_{W2}$ , with  $800\text{ }^{\circ}\text{C} \leq T_{W2} \leq 1040\text{ }^{\circ}\text{C}$ , preferably  $800\text{ }^{\circ}\text{C} \leq T_{W2} \leq 900\text{ }^{\circ}\text{C}$ , and/or  $5\text{ min} \leq t_{W2} \leq 200\text{ min}$ , preferably  $5\text{ min} \leq t_{W2} \leq 30\text{ min}$ .
14. A method for producing a dental product with a lithium silicate glass-ceramic blank produced firstly according to any one of claims 11 to 13 and then dental product is produced from the lithium silicate glass-ceramic blank by means of a CAD/CAM method.