HU000027960T2

(19) **HU**

(11) Lajstromszám: **E 027 960**

(13) **T2**

MAGYARORSZÁG
Szellemi Tulajdon Nemzeti Hivatala

EURÓPAI SZABADALOM
SZÖVEGÉNEK FORDÍTÁSA

(21) Magyar ügyszám: **E 13 179985**
(22) A bejelentés napja: **2011. 04. 18.**

(96) Az európai bejelentés bejelentési száma:
EP 20110179985
(97) Az európai bejelentés közzétételi adatai:
EP 2662343 A1 **2013. 11. 13.**
(97) Az európai szabadalom megadásának meghirdetési adatai:
EP 2662343 B1 **2015. 08. 12.**

(51) Int. Cl.: ***C03C 30/95*** *(2006.01)*
A61K 6/02 *(2006.01)*
C03C 10/12 *(2006.01)*
A61K 60/27 *(2006.01)*

(30) Elsőbbségi adatok:
10160222 **2010. 04. 16.** **EP**

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(54) **ZrO2-tartalmú lítiumszilikát-üvegkerámia és -üveg**

EP13179985.0
P 92768

Lithium silicate glass ceramic and glass with ZrO_2 content

The invention relates to the use of lithium silicate glass ceramic and glass which comprise ZrO_2 for the preparation of dental restorations.

Zirconium oxide ceramics are characterized by excellent biocompatibility and outstanding mechanical properties, which is why in the past they have increasingly been used as a material for implants and prostheses, but also as framework materials for dental restorations. Ceramics based on partially stabilized zirconium oxide are primarily used for this.

In many cases it is desirable to alter the surface of the zirconium oxide ceramic by coating it with a different material. Specifically when preparing dental restorations based on zirconium oxide ceramic, such a coating is regularly used to give the restoration the desired visual properties.

Glass ceramics have already been used in the past to coat or veneer oxide ceramics, such as zirconium oxide ceramics. These include feldspar-based ceramics or fluoroapatite glass ceramics.

Lithium disilicate glass ceramics are also known which, because of their high translucency and very good mechanical properties, are used in particular in the dental field and primarily for preparing dental crowns and small bridges.

EP 1 505 041 describes lithium silicate glass ceramics which can additionally contain 0 to 2 wt.-% ZrO_2. These are processed into the desired dental restorations in particular in the form of lithium metasilicate glass ceramics by means of CAD/CAM methods, wherein a subsequent heat treatment effects the conversion of the metasilicate phase to the high-strength disilicate phase. The glass ceramics can also be used for pressing over ceramic restorations.

EP 1 688 398 describes similar lithium silicate glass ceramics which are substantially free of ZnO and in addition to other components can contain 0 to 4 wt.-% ZrO_2. To achieve high strengths, however, small quantities of from 0 to 2 wt.-% ZrO_2 are preferred. These glass ceramics also serve in particular to prepare dental restorations after mechanical processing by means of CAD/CAM.

However, these lithium silicate glass ceramics known from the state of the art have the disadvantage that they are not suitable for coating zirconium oxide ceramic in particular by means of a pressing-on in the viscous state, since after the pressing-on in the viscous flow process cracks and flaws form in the glass ceramic. Thus, such a composite does not have the mechanical properties that are indispensable specifically for use as dental restoration material.

Glass ceramics with lithium disilicate as main crystal phase which are to be suitable for veneering dental restorations comprising yttrium-stabilized zirconium dioxide are also known from WO 2008/106958. However, these glass ceramics contain quantities of only up to 6.0 wt.-% of ZrO_2 and substantial quantities of Na_2O. The ZrO_2 present acts merely as a standard nucleating agent together with an optionally present further

nucleating agent such as TiO_2 in order to effect the formation of the desired lithium disilicate crystal phase.

In view of the above-described disadvantages of the already known glass ceramics, the object of the invention is to provide a glass ceramic which can be coated onto a zirconium oxide ceramic in particular by pressing it on in the viscous state and in the process forms a coating substantially free of cracks and flaws. Moreover, the glass ceramic should be capable of forming a solid bond with the zirconium oxide ceramic to be coated, and it should have visual and mechanical properties enabling it to be used in particular as a coating material for dental restorations but also as a material for preparing dental restorations.

This object is achieved by the use of a lithium silicate glass ceramic or a lithium silicate glass with nuclei according to any one of claims 1 to 14. Also a subject of the invention is the process for preparing a dental restoration according to claims 15 and 16.

The lithium silicate glass ceramic used according to the invention is characterized in that it comprises 8.0 to 16.0 wt.-% ZrO_2 and lithium metasilicate as main crystal phase.

In a further preferred embodiment, the glass ceramic comprises in particular 10.0 to 16.0 wt.-% ZrO_2.

Further, a glass ceramic which comprises 55.0 to 71.0, preferably 60.0 to 71.0 and in particular 60 to 69 wt.-% SiO_2 is preferred.

In addition, a glass ceramic which comprises 9.0 to 17.0 and in particular 11 to 15 wt.-% Li_2O is preferred.

Furthermore, it has proven particularly preferable if the glass ceramic comprises 0.5 to 12.0 and in particular 2.5 to 7.0 wt.-% nucleating agents. Preferred nucleating agents are selected from P_2O_5, TiO_2, Nb_2O_5, metals, e.g. Pt, Pd, Au and Ag, or mixtures

thereof. Particularly preferably, the glass ceramic comprises P_2O_5 as nucleating agent. Surprisingly, P_2O_5 as nucleating agent in particular effects the formation of desired lithium disilicate crystals while largely preventing the formation of ZrO_2-containing crystal phases which could cause a substantial deterioration in translucency. Through its use the formation of other undesired secondary crystal phases is apparently also largely prevented.

The glass ceramic used according to the invention preferably comprises further alkali metal oxide in a quantity of from 1.0 to 7.0, preferably 2.0 to 7.0 and particularly preferably 2.0 to 5.0 wt.-%. The term "further alkali metal oxide" denotes alkali metal oxide with the exception of Li_2O. The further alkali metal oxide is in particular K_2O, Cs_2O and/or Rb_2O and is particularly preferably K_2O. It is assumed that the use of K_2O contributes to the strengthening of the glass network compared with the Na_2O used in conventional glass ceramics. It is preferred that the glass ceramic comprises less than 2.0, in particular less than 1.0, preferably less than 0.5 and particularly preferably essentially no Na_2O.

It is further preferred that the glass ceramic comprises up to 5.0 wt.-% alkaline earth metal oxide, wherein the alkaline earth metal oxide is in particular CaO, BaO, MgO, SrO or a mixture thereof.

Further, a glass ceramic which comprises 0.2 to 10.0, in particular 2.5 to 7.0 and preferably 2.5 to 3.5 wt.-% oxide of trivalent elements is preferred, wherein this oxide is selected in particular from Al_2O_3, Y_2O_3, La_2O_3, Bi_2O_3 and mixtures thereof, and preferably is Al_2O_3.

A glass ceramic which comprises at least one and preferably all of the following components is particularly preferred:

Component	wt.-%
SiO_2	55.0 to 71.0

Li_2O	9.0 to 17.0
K_2O	1.0 to 7.0, in particular 2.0 to 5.0
Al_2O_3	0.5 to 5.0, in particular 2.5 to 3.5
P_2O_5	0.5 to 12.0, in particular 2.5 to 7.0
ZrO_2	8.0 to 16.0.

The glass ceramic used according to the invention can moreover also comprise additional components which are selected in particular from further oxides of tetravalent elements, further oxides of pentavalent elements, oxides of hexavalent elements, melt accelerators, colourants and fluorescent agents.

The term "further oxides of tetravalent elements" denotes oxides of tetravalent elements with the exception of SiO_2 and ZrO_2. Examples of further oxides of tetravalent elements are SnO_2 and GeO_2.

The term "further oxides of pentavalent elements" denotes oxides of pentavalent elements with the exception of P_2O_5. An example of a further oxide of pentavalent elements is Bi_2O_5.

Examples of oxides of hexavalent elements are WO_3 and MoO_3.

A glass ceramic which comprises at least one further oxide of tetravalent elements, one further oxide of pentavalent elements or one oxide of hexavalent elements is preferred.

Examples of melt accelerators are fluorides.

Examples of colourants and fluorescent agents are oxides of d- and f-elements, such as e.g. the oxides of Ti, Sc, Mn, Fe, Ag, Ta, W, Ce, Pr, Nd, Tb, Er and Yb.

The term "main crystal phase" used below denotes the crystal phase which has the highest proportion by volume compared with other crystal phases.

The glass ceramic used according to the invention comprises lithium metasilicate as main crystal phase. The glass ceramic

in particular comprises more than 10 vol.-%, preferably more than 20 vol.-% and particularly preferably more than 30 vol.-% of lithium metasilicate crystals, relative to the total glass ceramic.

The glass ceramic can be converted by heat treatment to a glass ceramic which comprises lithium disilicate as main crystal phase. In particular the glass ceramic comprises more than 10 vol.-%, preferably more than 20 vol.-% and particularly preferably more than 30 vol.-% of lithium disilicate crystals, relative to the total glass ceramic.

The lithium disilicate glass ceramic shows particularly good mechanical properties and can be produced by heat treatment of the lithium metasilicate glass ceramic used according to the invention.

It was surprisingly shown that, despite its high ZrO_2 content, the lithium disilicate glass ceramic has advantageous mechanical parameters, such as high fracture toughness values, and can be applied to zirconium oxide ceramic in the viscous state by sintering-on or in particular pressing-on, without resultant stresses in the glass ceramic which manifest themselves in cracks or flaws. It is particularly surprising that these very good mechanical properties are achieved although the structure of the glass ceramic has lithium disilicate crystals which are not normally cross-linked to one another. On the other hand, such a cross-linking occurs with the known lithium disilicate glass ceramics and it is regarded as a key reason for their high strengths. It is currently assumed that the ZrO_2 in the glass ceramic used according to the invention, unlike in known products, does not serve as a nucleating agent for other crystal phases, but rather strengthens the glass network via Zr-O polyhedra embedded therein. These polyhedra can be $[ZrO_{6/2}]^{2-}$ or $[ZrO_{8/2}]^{4-}$ structural units which function as network formers or network modifiers.

It is also surprising that, despite its high ZrO_2 content, the lithium disilicate glass ceramic has a high translucency and

that no amorphous-amorphous phase separation occurs and that it can thus be used for the aesthetically pleasing coating of in particular dental restorations based on zirconium oxide ceramic.

The lithium disilicate crystals present in the lithium disilicate glass ceramic have in particular the form of small plates. It is assumed that this special morphology allows the crack-free material bond with zirconium oxide ceramics. The build-up of critical stresses in the material bond during the thermal cooling phase seems to be less strongly pronounced in the small-plate shaped crystal form than in lithium disilicate glass ceramics with elongated or needle-shaped crystals. In addition, a good fracture toughness, expressed by the K_{IC} value, is achieved with the small-plate shaped crystal morphology.

The lithium disilicate glass ceramic has in particular a fracture toughness, measured as K_{IC} value, of at least 1.5 $MPa \cdot m^{0.5}$ and in particular more than 1.8 $MPa \cdot m^{0.5}$. Furthermore, it has a high biaxial fracture toughness of preferably from 200 to 500 MPa. Moreover, it shows a high chemical resistance which was determined by mass loss after storage in acetic acid. The chemical resistance is in particular less than 60 $\mu g/cm^2$. Finally, it has a linear coefficient of thermal expansion of in particular less than 10.3 x $10^{-6}K^{-1}$ m/m, measured in the range of from 100 to 500°C, which is thus as a rule smaller than that of the zirconium oxide ceramic to be coated.

The invention also relates to the use of a lithium silicate glass with nuclei that are suitable for forming lithium metasilicate as main crystalline phase, wherein the glass comprises the components of the above-described glass ceramics used according to the invention. This glass thus comprises 8.0 to 16.0 wt.-% ZrO_2. With regard to preferred embodiments of this glass, reference is made to the above-described preferred embodiments of the glass ceramics according to the invention.

The glass having nuclei used according to the invention can be produced by heat treatment of a starting glass of corresponding composition. By a further heat treatment the

lithium metasilicate glass ceramic used according to the invention can then be formed, which in turn can be converted into the lithium disilicate glass ceramic described above by further heat treatment. The starting glass, the glass with nuclei and the lithium metasilicate glass ceramic can consequently be seen as precursors for the production of the high-strength lithium disilicate glass ceramic.

The glass ceramic used according to the invention and the glass used according to the invention are present in particular in the form of powders or blanks, as they can easily be further processed in these forms. They can, however, also be present in the form of dental restorations, such as inlays, onlays, crowns, veneers, or abutments.

The glass ceramic used according to the invention and the glass with nuclei used according to the invention can be produced by a process, in which a starting glass with the components of the glass ceramic or the glass is subjected to at least one heat treatment in the range of from 450 to 950°C.

The starting glass therefore comprises 8.0 to 16.0 wt.-% ZrO_2. In addition, it preferably also comprises suitable quantities of SiO_2 and Li_2O in order to make the formation of a lithium silicate glass ceramic possible. Furthermore, the starting glass can also comprise further components, such as are given above for the lithium silicate glass ceramic used according to the invention. Those embodiments are preferred which are also stated as preferred for the glass ceramic.

To prepare the starting glass, the procedure is in particular that a mixture of suitable starting materials, such as e.g. carbonates, oxides, phosphates and fluorides, is melted at temperatures of in particular from 1300 to 1600°C for 2 to 10 h. To achieve a particularly high homogeneity, the obtained glass melt is poured into water in order to form a glass granulate, and the obtained granulate is then melted again.

The melt can then be poured into moulds to produce blanks of the starting glass, so-called solid glass blanks or monolithic blanks.

It is also possible to pour the melt into water again in order to prepare a granulate. This granulate can then be pressed, after grinding and optionally adding of further components, such as colourants and fluorescent agents, to form a blank, a so-called powder green compact.

Finally, the starting glass can also be processed to form a powder after granulation.

The starting glass is then subjected, e.g. in the form of a solid glass blank, a powder green compact or in the form of a powder, to at least one heat treatment in the range of from 450 to 950°C. It is preferred that a first heat treatment is initially carried out at a temperature in the range of from 500 to 600°C to prepare a glass with nuclei which are suitable for forming lithium metasilicate crystals. This glass can then preferably be subjected to at least one further temperature treatment at a higher temperature and in particular more than 570°C to effect crystallization of lithium metasilicate.

Dental restorations, such as inlays, onlays, crowns, veneers or abutments, can be prepared from the glass ceramics used according to the invention and the glasses used according to the invention. In this connection the glass ceramic or the glass is shaped to the desired dental restoration by means of pressing. The pressing is usually conducted at elevated pressure and elevated temperature. For the pressing in particular the glass with nuclei used according to the invention and the lithium metasilicate glass ceramic used according to the invention can be used in a suitable manner, e.g. in the form of blanks. After preparation of the dental restoration of the desired shape by pressing it is possible to heat treat the restoration to convert precursors used, such as glass with nuclei or lithium metasilicate glass ceramic, into lithium disilicate glass ceramic.

The glass ceramic used according to the invention and the glass used according to the invention are also suitable for coating zirconium oxide ceramics.

For coating of zirconium oxide ceramic, the glass ceramic or the glass can be applied to the zirconium oxide ceramic and subjected to increased temperature.

This can take place in particular by sintering-on and preferably by pressing-on. With the sintering-on, the glass ceramic or the glass is applied to the ceramic to be coated in the usual way, e.g. as powder, and then sintered at increased temperature. With the preferred pressing-on, the glass ceramic or the glass is pressed on, e.g. in the form of powder green compacts or monolithic blanks, at an increased temperature of e.g. from 700 to 1200°C, applying pressure, e.g. 2 to 10 bar. The methods described in EP 231 773 and the press furnace disclosed there can be used in particular for this. A suitable furnace is e.g. the Programat EP 5000 from Ivoclar Vivadent AG, Liechtenstein.

It is preferred that, after conclusion of the coating process, the above described glass ceramic is present with lithium disilicate as main crystal phase, as it has particularly good properties. It is surprisingly shown that the glass ceramic has practically no flaws and cracks once it has been coated onto the zirconium oxide ceramic, and a solid bond between glass ceramic and ceramic is achieved.

It is preferred that the zirconium oxide ceramic comprises at least one oxide of Ce, Y, Sr, Ca or Mg for stabilizing the tetragonal phase. The zirconium oxide ceramic can also be present in the form of a composite with other inorganic components.

It is surprising that no cracks occur in the glass ceramic in the bond between the above described lithium disilicate glass ceramic and the zirconium oxide ceramic. It is presumed that in particular the special small-plate shaped morphology of the

lithium disilicate crystals is of importance for this. The build-up of critical stress in the material bond during the thermal cooling phase seems to be less strongly pronounced in the small-plate shaped crystal form than in lithium disilicate glass ceramics with elongated or needle-shaped crystals. In addition a good fracture toughness of up to 2.1 $MPa \cdot m^{0.5}$ is achieved in particular with the small-plate shaped crystal morphology, although a direct cross-linking of the lithium disilicate crystals is essentially not to be seen in the structure. The coated zirconium oxide ceramic is thus a strong compound between high-strength and high-toughness zirconium oxide ceramic on the one hand and tough glass ceramic on the other, which is why this compound can absorb high loads in the chewing cycle. The glass ceramic can thus advantageously also be used directly in the coating of long-span bridges with more than three members based on zirconium oxide ceramic.

Finally, the glasses and glass ceramics used according to the invention can also be mixed with other glasses and glass ceramics to give dental materials having desirably adjusted properties. The glass and glass ceramic used according to the invention can therefore in particular be used as main component of an inorganic-inorganic composite or can be used in combination with a multitude of other glasses and/or glass ceramics. These composites or combinations are preferably used as dental materials. It is particularly preferred to use the composites and combinations in the form of sintered blanks. Examples of other glasses and glass ceramics for producing inorganic-inorganic composites and mixtures are disclosed in DE 43 14 817, DE 44 23 793, DE 44 28 839, DE 196 47 739, DE 197 25 552 and DE 100 31 431. These glasses and glass ceramics belong to the silicate, borate, phosphate or aluminosilicate group. Preferred glasses and glass ceramics are of the SiO_2-Al_2O_3-K_2O type (with cubic or tetragonal leucite crystals), SiO_2-B_2O_3-Na_2O type, alkali-silicate type, alkali- zinc-silicate type, silico-phosphate type and/or SiO_2-ZrO_2 type. By mixing such glasses and/or glass ceramics with the glasses and/or glass ceramics used according to the invention it is for example possible to

adjust the thermal coefficient of expansion in the desired manner in a broad range of 6 to $20*10^{-6}*1/K$.

The invention is described in further detail below with reference to examples.

Examples

Examples 1 to 23 - Composition and crystal phases

A total of 23 glasses and glass ceramics with the composition given in tables I to IV were prepared by melting corresponding starting glasses followed by heat treatment for controlled nucleation and crystallization.

For this, the starting glasses were firstly melted in a 100 to 200 g scale from usual raw materials at 1400 to 1500°C and transformed into glass frits by pouring them into water. These glass frits were then melted a second time at 1450 to 1550°C for 1 to 3 h for the homogenization. The obtained glass melts were poured into pre-heated moulds to produce glass monoliths. These glass monoliths were transformed into glasses and glass ceramics by thermal treatment.

The applied thermal treatment for the controlled nucleation and controlled crystallization is given in table V for selected examples. The first heat treatment in the range of from 500 to 560°C usually led to the formation of lithium silicate glasses with nuclei for lithium metasilicate or lithium disilicate crystals, the second heat treatment at 650 to 710°C to the formation of lithium metasilicate glass ceramics and the third heat treatment in the range of from 800 to 920°C to the formation of lithium disilicate glass ceramics.

In some examples, a second non-isothermal heat treatment with simultaneous analysis of the formed crystal phases was carried

out at the respectively given temperature by high-temperature X-ray diffraction (HT-XRD) after a first heat treatment.

The crystal phases obtained after conclusion of all the heat treatments are also listed in table V. Surprisingly, glass ceramics with lithium disilicate as main crystal phase were always obtained. Examples 4 and 5 were additionally repeated, by carrying out only the first and second heat treatment. In this way, glass ceramics with lithium metasilicate as main crystal phase were produced.

Example 24 - Glass and glass ceramic blanks

A glass with the composition according to example 4 was prepared by mixing corresponding raw materials in the form of oxides and carbonates for 30 min in a Turbula mixer and then melting the mixture at 1450°C for 120 min in a platinum crucible. The melt was poured into water in order to obtain a finely divided glass granulate. This glass granulate material was melted again at 1530°C for 150 min in order to obtain a glass melt with particularly high homogeneity. The temperature was reduced to 1500°C for 30 min and cylindrical glass blanks with a diameter of 12.5 mm were then poured into pre-heated, separable steel moulds or graphite moulds. The obtained glass cylinders were then stress-relieved at 550°C. A glass with nuclei for lithium metasilicate or lithium disilicate crystals was obtained.

Figure 1 shows the result of the differential thermal analysis (DSC) of a pounded glass cylinder.

Figure 2 shows, using high-temperature X-ray diffraction (HT-XRD) of a glass cylinder, the dependence of the formation of lithium metasilicate (Li_2SiO_3) and lithium disilicate ($Li_2Si_2O_5$) from the temperature.

The glass cylinders were then subjected to a first crystallization at 680 to 700°C for 20 min. The heating rate was 15°C per minute. The glass cylinders were then subjected to a second crystallization at 850 to 880°C for 30 min. After this treatment, the crystal phase analysis showed a glass ceramic with lithium disilicate as main crystal phase as well as small proportions of lithium metasilicate and lithium phosphate as secondary phases.

Figure 3 shows a scanning electron microscopy (SEM) photograph of a crystallized cylinder which has been polished and etched for 30 s with HF vapour.

The crystallized cylinders were moreover further processed by hot-pressing at a pressing temperature of 910°C using an EP600 press furnace, Ivoclar Vivadent AG, to form testpieces. The properties of these testpieces were as follows:

Colour:	white, translucent without fluorescence
Solubility:	24 $\mu g/cm^2$ (according to ISO 6872 of September 1, 2008)
Biaxial strength:	420 MPa (according to ISO 6872 of September 1, 2008)
Fracture toughness:	2.0 $MPam^{0.5}$ (determined as K_{Ic} value using the SEVNB method according to ISO 6872 of September 1, 2008)
Coefficient of thermal expansion:	$9.9*10^{-6}*1/K$ (in the range 100 to 500°C)

Example 25 - Glass and glass ceramic blanks

Example 24 was repeated with the difference that a glass with the composition according to example 18 was used as a starting material. The obtained crystallized cylinders were further

processed into testpieces by hot-pressing at a temperature of 905°C. The properties of these testpieces were as follows:

Colour:	tooth coloured, translucent with tooth-like fluorescence
Solubility:	30 $\mu g/cm^2$ (according to ISO 6872 of September 1, 2008)
Biaxial strength:	405 MPa (according to ISO 6872 of September 1, 2008)
Coefficient of thermal expansion:	$9.9*10^{-6}*1/K$ (in the range 100 to 500°C)

Example 26 - Glass ceramic blank (powder green compact)

Analogously to examples 1 to 23, a starting glass with the composition according to example 19 was melted twice. However, the glass was then not poured into steel moulds, but quenched in water in order to obtain a finely divided glass granulate. The glass granulate material was thermally treated at 550°C for 20 min and then at 680°C for 20 min in order to effect the nucleation and the first crystallization. The thus pre-treated granulate was dry-ground to an average grain size of 20 µm and mixed with 0.1 wt.-% of a ceramic colouring pigment. The mixture was moistened with some water and pressed to form a powder green compact at a pressing pressure of 20 MPa. The powder green compact was sintered at 850°C for 30 min. The crystal phase analysis of the sintered blank showed lithium disilicate as main crystal phase as well as in each case small proportions of lithium metasilicate and lithium phosphate as secondary phases.

The sintered blanks were further processed into testpieces by hot-pressing at 905°C using the EP600 press furnace (Ivoclar Vivadent AG). The properties of the testpieces were as follows:

Colour:	tooth coloured, translucent and tooth-like fluorescence
Biaxial strength:	302 MPa (according to ISO 6872 of September 1, 2008)

Example 27 - Direct preparation of dental restorations by hot-pressing

(A) Blanks of glass with nuclei

First of all glasses having the composition according to examples 2, 3 and 4 were prepared by mixing corresponding raw materials in the form of oxides and carbonates for 30 min in a Turbola mixer and then melting the mixture at 1450°C for 120 min in a platinum crucible. The melts were poured into water in order to obtain finely divided glass granulates. These glass granulates were melted again at 1530°C for 150 min in order to obtain glass melts with particularly high homogeneity. The temperature was reduced to 1500°C for 30 min and subsequently a) rectangular glass blanks (12.5 mm x 14 mm x 40 mm) and b) cylindrical glass blanks with a diameter of 12.5 mm were then poured into pre-heated, separable steel moulds or graphite moulds. The obtained rectangular glass blocks or glass cylinders were then heat-treated in the range of 500 to 560°C depending on the composition to produce nuclei for lithium metasilicate and/or lithium disilicate crystals und to stress-relieve the glass.

The obtained blanks with nuclei were processed according to the following alternatives to restorations.

(B) Hot-pressing of glass with nuclei or lithium metasilicate glass ceramic

i) The glass cylinders with nuclei (A) were processed by hot-pressing at a temperature of 900-950°C by means of a pressing furnace EP600, Ivoclar Vivadent AG, to give dental restorations, e.g. inlays, onlays, veneers, partial crowns and crowns. In the restorations lithium disilicate could be detected as main crystalline phase.

ii) The glass cylinders with nuclei (A) were subjected to a first crystallization at 650 to 750°C for 20 minutes. The heating-up rate was 15°C per minute. After this first crystallisation lithium metasilicate was detected as main crystalline phase. Through hot-pressing of the lithium metasilicate glass cylinders at a pressing temperature of 900-950°C using a pressing furnace EP600, Ivoclar Vivadent AG, it was possible to produce dental restorations, e.g. inlays, onlays, veneers, partial crowns and crowns. The hot-pressing converted lithium metasilicate into lithium disilicate.

Table I

	1	2	3	4	5	6
SiO_2	63.8	67.9	66.4	65.0	63.5	62.0
K_2O	3.0	3.7	3.6	3.5	3.4	3.4
Li_2O	13.6	14.1	13.8	13.5	13.2	12.9
Al_2O_3	3.0	3.2	3.2	3.1	3.0	2.9
P_2O_5	3.0	3.1	3.0	2.9	2.9	2.8
ZrO_2	9.6	8.0	10.0	12.0	14.0	16.0
MoO_3	4.0					
	100.0	100.0	100.0	100.0	100.0	100.0

Table II

	7	8	9	10	11	12	13	14	15
SiO_2	69.8	64.1	65.2	60.5	66.4	55.0	70.1	64.3	64.2
K_2O	2.0	5.0	3.5	3.3		4.0	3.6	3.0	1.0
Li_2O	16.0	13.3	12.0	15.0	13.6	15.0	9.0	13.2	13.2
Na_2O							0.1		
CaO						2.0			
MgO							0.1		
SrO							0.1		1.0
Al_2O_3	0.2	5.0	3.1	2.9	3.0	4.0	3.5	2.9	0.5
La_2O_3									
Y_2O_3									6.5
P_2O_5	3.3	2.9	4.1	5.0	3.0	12.0	3.5	2.9	3.5
ZrO_2	8.6	9.7	12.1	13.3	10.0	8.0	10.0	9.7	10.1
Cs_2O					4.0			4.0	
VO_2	0.1								
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table III

	16	17	18	19
SiO_2	61.3	62.6	64.9	64.9
K_2O	3.3	5.0	3.5	3.5
Li_2O	12.7	12.7	13.5	13.5
CaO	3.0			
Al_2O_3	2.9	2.9	3.1	3.1
P_2O_5	7.0	3.5	3.0	3.0
ZrO_2	9.0	11.3	10.4	10.9
F	0.5			
MnO_2	0.2			
Fe_2O_3	0.1			
V_2O_5			0.1	
Tb_4O_7		0.4	0.5	0.5
CeO2		1.3	1.0	0.6
Er_2O_3		0.3		
	100.0	100.0	100.0	100.0

Table IV

	20	21	22	23
SiO_2	66.4	63.8	64.5	63.8
K_2O		3.0	3.2	3.0
Li_2O	13.6	13.6	13.8	13.6
Rb_2O	4.0			
BaO			2.0	
Al_2O_3	3.0	3.0	3.0	3.0
Bi_2O_3				4.0
P_2O_5	3.0	3.0	3.5	3.0
ZrO_2	10.0	9.6	10.0	9.6
WO_3		4.0		
	100.0	100.0	100.0	100.0

Table V

Glass ceramic, no.	Thermal treatment (°C/min) or HT-XRD	Crystal phases MP = main phase SP = secondary phase(s)
2	500/10, 650/20, 840/7	MP:$Li_2Si_2O_5$ SP:Li_3PO_4 Li_2SiO_3
3	500/10, 650/20, 840/7	MP:$Li_2Si_2O_5$ SP:Li_3PO_4,Li_2SiO_3; Li_4SiO_4
4	540/10, 690/20	MP: Li_2SiO_3 SP: none
4	540/10, 650/20, 840/7	MP:$Li_2Si_2O_5$ SP:Li_2SiO_3; Li_4SiO_4
5	540/10, 710/20	MP: Li_2SiO_3 SP: none
5	540/10, 650/20, 840/7	MP:$Li_2Si_2O_5$ SP:Li_4SiO_4
6	560/10 and HT-XRD with cut-out at 860	MP:$Li_2Si_2O_5$ SP:Li_3PO_4, Li_2SiO_3
11	520/10, 650/20, 800/10	MP:$Li_2Si_2O_5$ SP:Li_3PO_4
12	HT-XRD with cut-out at 840	MP:$Li_2Si_2O_5$ SP:Li_3PO_4
20	520/10, 650/20, 800/10	MP:$Li_2Si_2O_5$ SP:Li_3PO_4
21	520/10, 650/20, 850/10	MP:$Li_2Si_2O_5$ SP:Li_3PO_4, Li_2SiO_3

In the HT-XRD analysis, a heating rate of approx. 2 K/min was used.

ZrO_2-tartalmú lítiumszilikát-üvegkerámia és -üveg

SZABADALMI IGÉNYPONTOK

1. Lítiumszilikát üvegkerámia alkalmazása - mely 8,0-16,0 tömeg% ZrO_2-t tartalmaz, és fő kristályos fázisként lítium-metaszilikátot tartalmaz – fogpótlások előállítására, ahol az üvegkerámiát sajtolással formázzuk a kívánt fogpótlássá.

2. A 2. igénypont szerinti alkalmazás, ahol az üvegkerámia több mint 10 térfogat% lítium-metaszilikát kristályt tartalmaz.

3. Az 1. igénypont szerinti alkalmazás, ahol az üvegkerámia több mint 20 térfogat%, és különösen előnyösen több mint 30 térfogat% lítium-metaszilikát kristály tartalommal rendelkezik.

4. Az 1-3. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia 55,0-71,0, és különösen 55,0-69,0 tömeg% SiO_2-t tartalmaz.

5. Az 1-4. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia, 0,5-12,0, és különösen 2,5-7,0 tömeg% magképző szert tartalmaz, ahol a magképző szer különösen a P_2O_5, TiO_2, Nb_2O_5 és/vagy fémek közül van kiválasztva, előnyösen P_2O_5.

6. Az 1-5. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia a Li_2O-n kívül további alkálifémoxidot tartalmaz, 1,0-7,0, előnyösen 2,0-7,0, és különösen előnyösen 2,0-5,0 tömeg% mennyiségben, ahol a további alkálifémoxid különösen a K_2O, Cs_2O és/vagy Rb_2O, és előnyösen a K_2O.

7. Az 1-6. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia legfeljebb 5,0 tömeg% alkáliföldfém-oxidot tartalmaz, ahol az alkáliföldfém-oxid előnyösen a CaO, BaO, MgO és/vagy SrO.

8. Az 1-7. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia 0,2-10,0, különösen 2,5-7,0 és előnyösen 2,5-3,5 tömeg% mennyiségben három vegyértékű elemek oxidjait tartalmazza, ahol a három vegyértékű elemek oxidja különösen Al_2O_3, Y_2O_3, La_2O_3 és/vagy Bi_2O_3, és előnyösen Al_2O_3.

9. Az 1-8. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia legalább egy további, négy vegyértékű elem oxidját, különösen SnO_2-t vagy GeO_2-t, egy további, öt vegyértékű elem oxidját, különösen Bi_2O_5-öt vagy egy hat vegyértékű elem egy oxidját, különösen WO_3-at vagy MoO_3-at tartalmazza.

10. Az 1-9. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia az alábbi komponensek közül legalább egyet, előnyösen mindegyiket tartalmazza:

Komponens	tömeg%
SiO_2	55,0 - 69,0
K_2O	1,0 - 5,0
Al_2O_3	0,5 - 3,5
P_2O_5	0,5 - 12,0, különösen 2,5 - 7,0.

11. Az 1-10. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia K_{Ic} értékként mért törési szilárdsága legalább 1,5 $MPa \cdot m^{0,5}$, és különösen több mint 1,8 $MPa \cdot m^{0,5}$.

12. Lítiumszilikát-üveg - mely a fő kristályos fázisként lítium-metaszilikát előállítására alkalmas magot tartalmaz, ahol az üveg az 1. vagy 4-10. igénypontok bármelyike szerinti üvegkerámia komponenseket tartalmazza – alkalmazása, fogpótlás előállítására, ahol az üveg sajtolással van a kívánt fogpótlás formára alakítva.

13. Az 1-12. igénypontok bármelyike szerinti alkalmazás, ahol az üvegkerámia vagy az üveg por vagy nyers munkadarab formájában van.

14. Az 1-13. igénypontok bármelyike szerinti alkalmazás, inlayek, onlayek, borítások, koronarészek, koronák, héjak vagy fogászati felépítmények előállítására.

15. Eljárás fogpótlás előállítására, ahol egy, az 1-11. vagy 13. igénypont szerinti üvegkerámiát vagy a 12. vagy 13. igénypont szerinti üveget sajtolással a kívánt fogpótlássá alakítjuk.

16. A 15. igénypont szerinti eljárás, üvegkerámia vagy üveg előállítására, ahol az üvegkerámia vagy üveg komponenseit tartalmazó kiindulási üveget legalább egy hőkezelésnek vetjük alá, 450-950°C hőmérsékleten.

A meghatalmazott

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Fig. 1

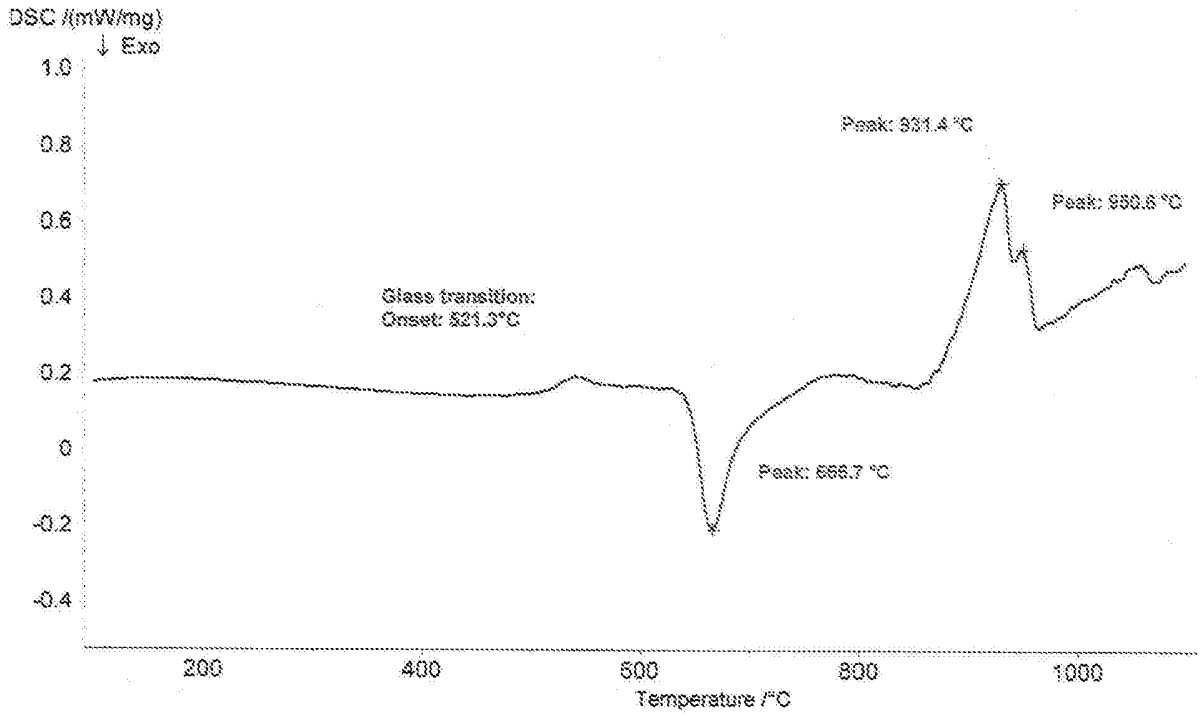
DSC /(mW/mg)
↓ Exo
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
Peak: 931.4 °C
Peak: 950.6 °C
Glass transition:
Onset: 521.3°C
Peak: 666.7 °C
200
400
600
800
1000
Temperature /°C

Fig. 2

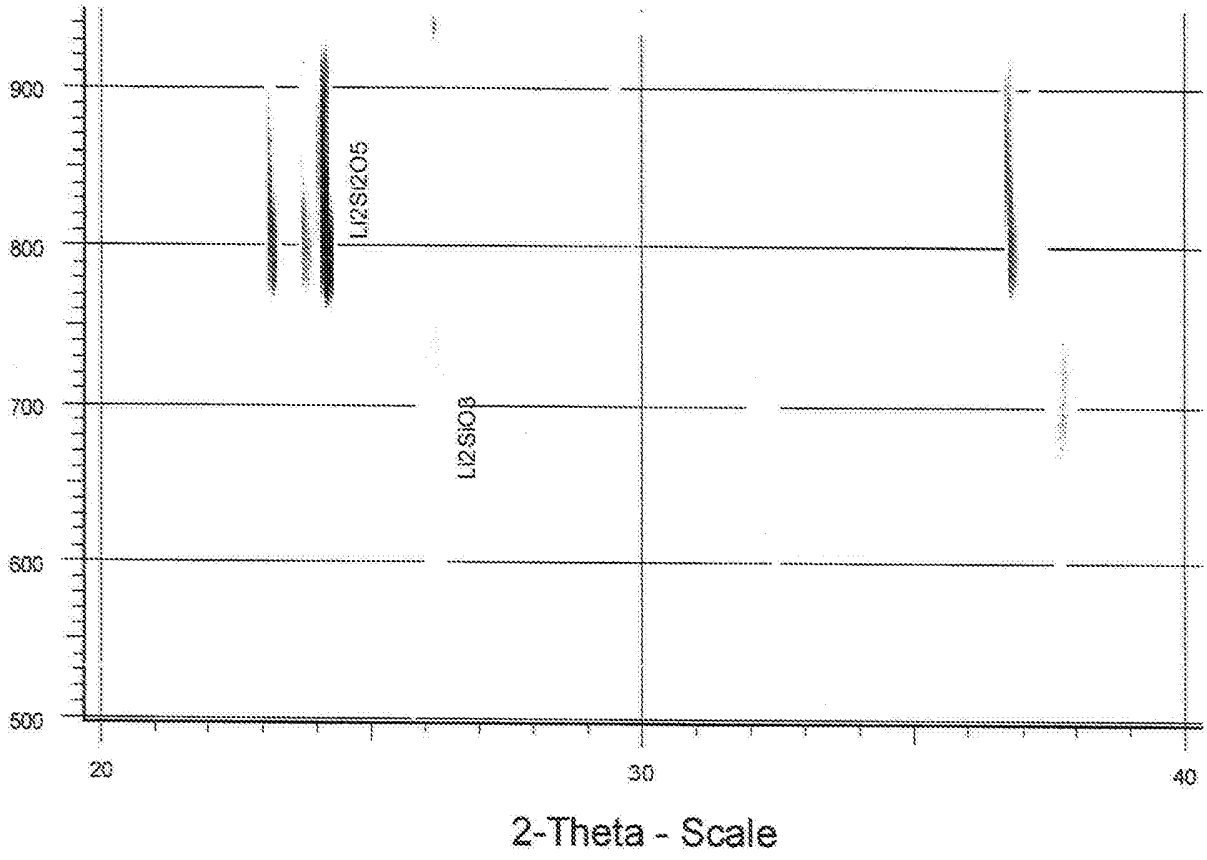

Fig. 3