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(54) Titre : VITROCERAMIQUE ET VERRE EN SILICATE DE LITHIUM, AYANT UN OXYDE METALLIQUE
TETRAVALENT
(54) Title: LITHIUM SILICATE GLASS CERAMIC AND GLASS WITH TETRAVALENT METAL OXIDE

(57) **Abrégé/Abstract:**

Lithium silicate glass ceramics generally possess desirable mechanical properties and have been used in the dental field for, e.g., dental crowns and bridges. They usually require heat treatments at more than 800°C to effect precipitation as the main crystal phase. The present invention relates to lithium silicate glass ceramics and glasses containing specific oxides of tetravalent elements which crystallize at low temperatures and are suitable in particular as dental materials. The lithium silicate glass ceramic may comprise: tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof, 67.0 to 79.0 wt.-% SiO_2 , at least 12.1 wt.-% Li_2O , 0 to 6.0 wt.-% Al_2O_3 , less than 0.1 wt.-% La_2O_3 , less than 1.0 wt.-% K_2O and less than 2.0 wt.-% Na_2O .

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Abstract

Lithium silicate glass ceramics generally possess desirable mechanical properties and have been used in the dental field for, e.g., dental crowns and bridges. They usually require heat treatments at more than 800°C to effect precipitation as the main crystal phase. The present invention relates to lithium silicate glass ceramics and glasses containing specific oxides of tetravalent elements which crystallize at low temperatures and are suitable in particular as dental materials. The lithium silicate glass ceramic may comprise: tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof, 67.0 to 79.0 wt.-% SiO_2 , at least 12.1 wt.-% Li_2O , 0 to 6.0 wt.-% Al_2O_3 , less than 0.1 wt.-% La_2O_3 , less than 1.0 wt.-% K_2O and less than 2.0 wt.-% Na_2O .

Lithium silicate glass ceramic and glass with tetravalent metal oxide

5 The invention relates to lithium silicate glass ceramic and glass which contain tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof and are particularly suitable for use in dentistry, preferably for the preparation of dental restorations.

10 Lithium silicate glass ceramics are characterized as a rule by very good mechanical properties, which is why they have been used for a long time in the dental field and there primarily for the preparation of dental crowns and small bridges. The known lithium silicate glass ceramics usually contain as main
15 components SiO_2 , Li_2O , Na_2O or K_2O , and nucleating agents such as P_2O_5 as well as additional components such as e.g. La_2O_3 .

DE 24 51 121 describes lithium disilicate glass ceramics which contain K_2O . They are prepared from corresponding nuclei-containing starting glasses which are heated to temperatures of from 850 to 870°C for the crystallization of lithium
5 disilicate. The purpose for which the glass ceramics are used is not disclosed.

EP 827 941 describes sinterable lithium disilicate glass ceramics for dental purposes, which also contain K_2O or Na_2O in
10 addition to La_2O_3 . The lithium disilicate crystal phase is produced at a temperature of 850°C.

Lithium disilicate glass ceramics which likewise contain La_2O_3 as well as K_2O are known from EP 916 625. A heat treatment is
15 carried out at 870°C for the formation of lithium disilicate.

EP 1 505 041 describes lithium silicate glass ceramics containing K_2O , which, when lithium metasilicate is present as main crystal phase, can be very satisfactorily machined e.g.
20 by means of CAD/CAM processes, in order to then be converted by further heat treatment at temperatures of from 830 to 850°C into high-strength lithium disilicate glass ceramics.

EP 1 688 398 describes similar K_2O -containing lithium silicate
25 glass ceramics which are moreover substantially free from ZnO . A heat treatment at 830 to 880°C is applied to them to produce lithium disilicate.

US 5,507,981 describes processes for producing dental
30 restorations and glass ceramics that can be used in these processes. These are in particular lithium disilicate glass ceramics with a low level of Li_2O which contain as a rule either Na_2O or K_2O .

35 US 6,455,451 relates to lithium disilicate glass ceramics which also contain K_2O in addition to Li_2O . However, the production of the desired lithium disilicate crystal phase requires high temperatures of from 800 to 1000°C.

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WO 2008/106958 discloses lithium disilicate glass ceramics for veneering zirconium oxide ceramics. The glass ceramics contain Na_2O and are produced by heat treatment of nuclei-containing glasses at 800 to 940°C.

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WO 2009/126317 describes GeO_2 -containing lithium metasilicate glass ceramics which contain K_2O and small quantities of SiO_2 . The glass ceramics are processed to form dental products primarily using machining.

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WO 2011/076422 relates to lithium disilicate glass ceramics which also contain K_2O in addition to high levels of ZrO_2 or HfO_2 . The crystallization of lithium disilicate takes place at high temperatures of from 800 to 1040°C.

15

Common to the known lithium disilicate glass ceramics is that they require heat treatments at more than 800°C in order to effect the precipitation of lithium disilicate as main crystal phase. A large quantity of energy is therefore also necessary for their production. Further, with the known glass ceramics the alkali metal oxides, such as in particular K_2O or Na_2O , as well as La_2O_3 , are as a rule present as essential components which are clearly required for the production of glass ceramics with the sought properties and in particular the formation of the sought lithium disilicate main crystal phase.

25

There is therefore a need for lithium silicate glass ceramics during the preparation of which the crystallization of lithium disilicate can be effected at lower temperatures. Further, they should also be able to be prepared without the alkali metal oxides, such as K_2O or Na_2O , as well as La_2O_3 , previously regarded as necessary, and be suitable in particular for the preparation of dental restorations primarily in view of their optical and mechanical properties.

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This application discloses lithium silicate glass ceramic which comprises tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof, 67.0 to 79.0 wt.-% SiO_2 , at least 12.1 wt.-% Li_2O , 0 to 6.0 wt.-% Al_2O_3 , less
5 than 0.1 wt.-% La_2O_3 , less than 1.0 wt.-% K_2O and less than 2.0 wt.-% Na_2O .

This application also discloses process for the preparation of a lithium silicate glass ceramic which comprises tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 ,
10 SnO_2 and mixtures thereof, at least 12.1 wt.-% Li_2O , less than 0.1 wt.-% La_2O_3 , less than 1.0 wt.-% K_2O and less than 2.0 wt.-% Na_2O , wherein (a) a starting glass which comprises the components of the glass ceramic is subjected to a heat treatment at a temperature of from 480 to 520°C for a period of from 10
15 min to 120 min in order to form a glass with nuclei which are suitable for forming lithium disilicate crystals, and (b) the glass with nuclei is subjected to a heat treatment at a temperature of from 640 to 740°C in order to form a glass ceramic with lithium disilicate as a main crystal phase.

20 This application also discloses use of a glass ceramic, a starting glass, or a glass with nuclei which are for forming lithium metasilicate and/or lithium disilicate crystals, wherein the glass ceramic or the glass comprises tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and
25 mixtures thereof, 67.0 to 79.0 wt.-% SiO_2 , at least 12.1 wt.-% Li_2O , less than 0.1 wt.-% La_2O_3 , less than 1.0 wt.-% K_2O and less than 2.0 wt.-% Na_2O , as dental material.

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The lithium silicate glass ceramic according to the invention is characterized in that it comprises

tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof,
at least 12.1 wt.-% Li_2O ,
less than 0.1 wt.-% La_2O_3 ,
less than 1.0 wt.-% K_2O and
less than 2.0 wt.-% Na_2O .

It is preferred that the glass ceramic comprises the tetravalent metal oxide or mixtures thereof in an amount of from 0.1 to 15, in particular 2.0 to 15.0, particularly preferred 2.0 to 11.0 and even more preferred 2.0 to 8.0 wt.-%.

It is particularly surprising that the formation of the glass ceramic according to the invention with lithium disilicate as main crystal phase is also achieved in the absence of various components regarded as necessary for conventional glass ceramics, such as alkali metal oxides, in particular K_2O , Na_2O and La_2O_3 , even at very low and thus advantageous crystallization temperatures of in particular from 640 to 740°C. The glass ceramic also has a combination of optical and mechanical properties as well as processing properties that are very advantageous for the use as dental material.

The glass ceramic according to the invention accordingly preferably comprises less than 0.5 and in particular less than 0.1 wt.-% K_2O . It is particularly preferably substantially free from K_2O .

A glass ceramic is also preferred which comprises less than 1.0, in particular less than 0.5 and preferably less than 0.1 wt.-% Na_2O and particularly preferred is substantially free from Na_2O .

5

Moreover, a glass ceramic which is substantially free from La_2O_3 is preferred.

A glass ceramic, excluding lithium silicate glass ceramic
10 which comprises at least 6.1 wt.-% ZrO_2 , is also preferred.

Further, a glass ceramic, excluding lithium silicate glass
ceramic which comprises at least 8.5 wt.-% transition metal
oxide selected from the group consisting of oxides of yttrium,
15 oxides of transition metals with an atomic number from 41 to
79 and mixtures of these oxides, is also preferred.

The glass ceramic according to the invention preferably
comprises 55.0 to 82.0, in particular 58.0 to 80.0, preferably
20 60.0 to 80.0 and particularly preferred 67.0 to 79.0 wt.-%
 SiO_2 .

It is also preferred that the glass ceramic comprises 12.5 to
20.0 and in particular 15.0 to 17.0 wt.-% Li_2O .

25

It is further preferred that the molar ratio between SiO_2 and
 Li_2O is from 1.7 to 3.1, in particular 1.75 to 3.0. It is very
surprising that the production of lithium disilicate is
achieved within this broad range. Specifically at ratios of
30 less than 2.0 conventional materials usually form lithium
metasilicate instead of lithium disilicate.

In a further preferred embodiment the molar ratio between SiO_2
and Li_2O is at least 2.2, in particular 2.3 to 2.5, and
35 preferably about 2.4, as a glass ceramic with particularly
high strength is thus obtained.

The glass ceramic according to the invention can also comprise
a nucleating agent. P_2O_5 is particularly preferably used for

this. The glass ceramic preferably comprises 0 to 10.0, in particular 0.5 to 9.0 and preferably 2.5 to 7.5 wt.-% P_2O_5 . However, metals in amounts of in particular from 0.005 to 0.5 wt.-%, such as in particular Ag, Au, Pt and Pd, can also be
5 used as nucleating agents.

In a further preferred embodiment, the glass ceramic comprises at least one and preferably all of the following components:

10	<u>Component</u>	<u>wt.-%</u>
	SiO_2	58.0 to 79.0
	Li_2O	12.5 to 20.0
	tetravalent metal oxide or mixtures	2.0 to 15.0
15	P_2O_5	0 to 7.0, in particular 0.5 to 7.0
	Al_2O_3	0 to 6.0, in particular 0.5 to 3.5.

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

25 Suitable oxides of divalent elements are in particular MgO , CaO , SrO , BaO and ZnO and preferably CaO .

Suitable oxides of trivalent elements are in particular Al_2O_3 , Y_2O_3 and Bi_2O_3 and mixtures thereof, and preferably Al_2O_3 ,
30 already mentioned above as a component.

The term "further oxides of pentavalent elements" refers to oxides of pentavalent elements with the exception of P_2O_5 . Examples of suitable further oxides of pentavalent elements
35 are Ta_2O_5 and Nb_2O_5 .

Examples of suitable oxides of hexavalent elements are WO_3 and MoO_3 .

A glass ceramic which comprises at least one oxide of divalent elements, at least one oxide of trivalent elements, at least one further oxide of pentavalent elements and/or at least one
5 oxide of hexavalent elements is preferred.

Examples of melt accelerators are fluorides.

Examples of colourants and fluorescent agents are oxides of d-
10 and f-elements, such as the oxides of Ti, V, Sc, Mn, Fe, Co, Ta, W, Ce, Pr, Nd, Tb, Er, Dy, Gd, Eu and Yb. Metal colloids, e.g. of Ag, Au and Pd, can also be used as colourants and in addition can also act as nucleating agents. These metal colloids can be formed e.g. by reduction of corresponding
15 oxides, chlorides or nitrates during the melting and crystallization processes. The metal colloids can be present in the glass ceramic in an amount of from 0.005 to 0.5 wt.-%.

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

The glass ceramic according to the invention has lithium metasilicate as main crystal phase in one embodiment. In
25 particular the glass ceramic comprises more than 5 vol.-%, preferably more than 10 vol.-% and particularly preferred more than 15 vol.-% lithium metasilicate crystals, relative to the total glass ceramic.

30 In a further particularly preferred embodiment, the glass ceramic has lithium disilicate as main crystal phase. In particular the glass ceramic comprises more than 10 vol.-%, preferably more than 20 vol.-% and particularly preferred more than 30 vol.-% lithium disilicate crystals, relative to the
35 total glass ceramic.

The lithium disilicate glass ceramic according to the invention is characterized by particularly good mechanical properties and can be produced e.g. by heat treatment of the

lithium metasilicate glass ceramic according to the invention. However, it can be formed in particular by heat treatment of a corresponding starting glass or of a corresponding lithium silicate glass with nuclei.

5

It has surprisingly been shown that the lithium disilicate glass ceramic according to the invention has very good mechanical and optical properties and processing properties even in the absence of components regarded as essential for conventional glass ceramics. The combination of its properties even allows it to be used as dental material and in particular material for the preparation of dental restorations.

The lithium disilicate glass ceramic according to the invention has in particular a fracture toughness, measured as K_{IC} value, of at least $1.8 \text{ MPa} \cdot \text{m}^{0.5}$ and in particular more than about $2.0 \text{ MPa} \cdot \text{m}^{0.5}$. This value was determined using the Vickers method and calculated using Niihara's equation.

The invention also relates to a lithium silicate glass with nuclei that are suitable for forming lithium metasilicate and/or lithium disilicate crystals, wherein the glass comprises the components of the above-described glass ceramics according to the invention. Thus this glass is characterized in that it comprises

tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof,
at least 12.1 wt.-% Li_2O ,
less than 0.1 wt.-% La_2O_3 ,
less than 1.0 wt.-% K_2O and
less than 2.0 wt.-% Na_2O .

In respect of preferred embodiments of this glass reference is made to the preferred embodiments described above of the glass ceramics according to the invention.

The glass with nuclei according to the invention can be produced by heat treatment of a correspondingly composed starting glass according to the invention. The lithium metasilicate glass ceramic according to the invention can then
5 be formed by a further heat treatment, and in turn be converted into the lithium disilicate glass ceramic according to the invention by further heat treatment, or the lithium disilicate glass ceramic according to the invention can also preferably be formed directly from the glass with nuclei. The
10 starting glass, the glass with nuclei and the lithium metasilicate glass ceramic can consequently be regarded as precursors to the production of the high-strength lithium disilicate glass ceramic.

15 The glass ceramics according to the invention and the glasses according to the invention are present in particular in the form of powders, granular material or blanks, e.g. monolithic blanks, such as platelets, cuboids or cylinders, or powder green compacts, in unsintered, partly sintered or densely-
20 sintered form. 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, facets or abutments.

25 The invention also relates to a process for the preparation of the glass ceramic according to the invention and the glass with nuclei according to the invention, wherein a correspondingly composed starting glass, the glass with nuclei according to the invention or the lithium metasilicate glass
30 ceramic according to the invention is subjected to at least one heat treatment in the range of from 450 to 950°C, in particular 450 to 750 and preferably 480 to 740°C.

The starting glass according to the invention is therefore
35 characterized in that it comprises

tetravalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof,
at least 12.1 wt.-% Li_2O ,

less than 0.1 wt.-% La_2O_3 ,
less than 1.0 wt.-% K_2O and
less than 2.0 wt.-% Na_2O .

5 In addition, it preferably also comprises suitable amounts of
 SiO_2 and Li_2O , in order to allow the formation of a lithium
silicate glass ceramic, and in particular a lithium disilicate
glass ceramic. Further, the starting glass can also comprise
10 still further components, such as are given above for the
lithium silicate glass ceramic according to the invention. All
those embodiments are preferred for the starting glass which
are also given as preferred for the glass ceramic.

With the process according to the invention, the glass with
15 nuclei is usually prepared by means of a heat treatment of the
starting glass at a temperature of in particular from 480 to
520°C. The lithium disilicate glass ceramic according to the
invention is then preferably produced from the glass with
nuclei through further heat treatment at usually 600 to 750
20 and in particular 640 to 740°C.

Thus, much lower temperatures are used according to the
invention for the crystallization of lithium disilicate than
with the conventional lithium disilicate glass ceramics. The
25 energy thus saved represents a clear advantage. Surprisingly,
this low crystallization temperature is also possible in the
absence of components, such as K_2O and Na_2O as well as La_2O_3 ,
regarded as essential for conventional glass ceramics.

30 To prepare the starting glass, the procedure is in particular
that a mixture of suitable starting materials, such as
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
35 glass melt is poured into water in order to form a granular
glass material, and the obtained granular material 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.

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

10

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

- 15 The starting glass, e.g. in the form of a solid glass blank, a powder green compact or in the form of a powder, is then subjected 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 480 to 520°C to prepare a glass according to the invention
- 20 with nuclei which are suitable for forming lithium metasilicate and/or lithium disilicate crystals. This first heat treatment is preferably carried out for a period of from 10 min to 120 min and in particular 10 min to 30 min. The glass with nuclei can then preferably be subjected to at least
- 25 one further temperature treatment at a higher temperature and in particular more than 570°C to effect crystallization of lithium metasilicate or lithium disilicate. This further heat treatment is preferably carried out for a period of from 10 min to 120 min, in particular 10 min to 60 min and
- 30 particularly preferably 10 min to 30 min. To crystallize lithium disilicate, the further heat treatment is usually carried out at 600 to 750 and in particular 640 to 740°C.

Therefore, in a preferred embodiment of the process

35

- (a) the starting glass is subjected to a heat treatment at a temperature of from 480 to 520°C in order to form the glass with nuclei, and

(b) the glass with nuclei is subjected to a heat treatment at a temperature of from 640 to 740°C in order to form the glass ceramic with lithium disilicate as main crystal phase.

5

The duration of the heat treatments carried out in (a) and (b) is preferably as given above.

10 The at least one heat treatment carried out in the process according to the invention can also take place during a hot pressing or sintering-on of the glass according to the invention or the glass ceramic according to the invention.

15 Dental restorations, such as bridges, inlays, onlays, crowns, veneers, facets or abutments, can be prepared from the glass ceramics according to the invention and the glasses according to the invention. The invention therefore also relates to their use for the preparation of dental restorations. It is preferred that the glass ceramic or the glass is shaped into
20 the desired dental restoration by pressing or machining.

The pressing is usually carried out at increased pressure and increased temperature. It is preferred that the pressing is carried out at a temperature of from 700 to 1200°C. It is
25 further preferred to carry out the pressing at a pressure of from 2 to 10 bar. During pressing, the desired shape change is achieved by viscous flow of the material used. The starting glass according to the invention and in particular the glass with nuclei according to the invention, the lithium
30 metasilicate glass ceramic according to the invention and the lithium disilicate glass ceramic according to the invention can be used for the pressing. The glasses and glass ceramics according to the invention can be used in particular in the form of blanks, e.g. solid blanks or powder green compacts,
35 e.g. in unsintered, partly sintered or densely-sintered form.

The machining is usually carried out by material removing processes and in particular by milling and/or grinding. It is particularly preferred that the machining is carried out as

part of a CAD/CAM process. The starting glass according to the invention, the glass with nuclei according to the invention, the lithium metasilicate glass ceramic according to the invention and the lithium disilicate glass ceramic according to the invention can be used for the machining. The glasses and glass ceramics according to the invention can be used in particular in the form of blanks, e.g. solid blanks or powder green compacts, e.g. in unsintered, partly sintered or densely-sintered form. The lithium metasilicate glass ceramic according to the invention and lithium disilicate glass ceramic according to the invention are preferably used for the machining. The lithium disilicate glass ceramic can also be used in a not yet fully crystallized form which was produced by heat treatment at a lower temperature. This has the advantage that an easier machining, and thus the use of simpler equipment for the machining, is possible. After the machining of such a partly crystallized material, the latter is usually subjected to a heat treatment at a higher temperature and in particular 640 to 740°C in order to effect further crystallization of lithium disilicate.

In general, after the preparation of the dental restoration shaped as desired by pressing or machining, the latter can also in particular be heat-treated in order to convert the precursors used, such as starting glass, glass with nuclei or lithium metasilicate glass ceramic, into lithium disilicate glass ceramic or to increase the crystallization of lithium disilicate or to reduce the porosity, e.g. of a porous powder green compact used.

However, the glass ceramic according to the invention and the glass according to the invention are also suitable as coating material of e.g. ceramics and glass ceramics. The invention is therefore also directed to the use of the glass according to the invention or the glass ceramic according to the invention for coating of in particular ceramics and glass ceramics.

The invention also relates to a process for coating ceramics and glass ceramics, wherein the glass ceramic according to the

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invention or the glass according to the invention is applied to the ceramic or glass ceramic and is subjected to increased temperature.

5 This can take place in particular by sintering-on and preferably by pressing-on. With sintering-on, the glass ceramic or the glass is applied to the material to be coated, such as ceramic or glass ceramic, in the usual way, e.g. as powder, and then sintered at increased temperature. With the
10 preferred pressing-on, the glass ceramic according to the invention or the glass according to the invention 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, and applying pressure, e.g. 2 to 10 bar. The methods
15 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 ProgramatTM EP 5000 from Ivoclar Vivadent AG, Liechtenstein.

It is preferred that, after conclusion of the coating process,
20 the glass ceramic according to the invention is present with lithium disilicate as main crystal phase, as it has particularly good properties.

Because of the above-described properties of the glass ceramic
25 according to the invention and the glass according to the invention as its precursor, these are suitable in particular for use in dentistry. A subject of the invention is therefore also the use of the glass ceramic according to the invention or the glass according to the invention as a dental material
30 and in particular for the preparation of dental restorations or as a coating material for dental restorations, such as crowns, bridges and abutments.

Finally, the glasses and glass ceramics according to the
35 invention can also be mixed together with other glasses and glass ceramics in order to produce dental materials with properties adjusted as desired. Compositions and in particular dental materials which comprise the glass according to the invention or the glass ceramic according to the invention in

combination with at least one other glass and/or one other glass ceramic therefore represent a further subject of the invention. The glass according to the invention or the glass ceramic according to the invention can therefore be used in particular as main component of an inorganic-inorganic composite or in combination with a plurality of other glasses and/or glass ceramics, wherein the composites or combinations can be used in particular as dental materials. The combinations or composites can particularly preferably be present in the form of sintered blanks. Examples of other glasses and glass ceramics for the preparation of inorganic-inorganic composites and of combinations are disclosed in DE 43 14 817, DE 44 23 793, DE 44 23 794, DE 44 28 839, DE 196 47 739, DE 197 25 553, DE 197 25 555, DE 100 31 431 and DE 10 2007 011 337. These glasses and glass ceramics belong to the group of silicates, borates, phosphates or aluminosilicates. Preferred glasses and glass ceramics are of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ type (with cubic or tetragonal leucite crystals), $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ type, alkali-silicate type, alkali-zinc-silicate type, silicophosphate type, $\text{SiO}_2\text{-ZrO}_2$ type and/or lithium-aluminosilicate type (with spodumene crystals). By mixing such glasses or glass ceramics with the glasses and/or glass ceramics according to the invention, for example the coefficient of thermal expansion can be adjusted as desired in a broad range of from 6 to $20 \cdot 10^{-6} \text{ K}^{-1}$.

The invention is explained in more detail below by means of examples.

ExamplesExamples 1 to 14 - Composition and crystal phases

- 5 A total of 14 glasses and glass ceramics according to the invention with the composition given in Table I were prepared by melting corresponding starting glasses followed by heat treatment for controlled nucleation and crystallization.
- 10 For this, the starting glasses weighing from 100 to 200 g were first melted from customary raw materials at 1400 to 1500°C, wherein the melting was very easily possible without formation of bubbles or streaks. By pouring the starting glasses into water, glass frits were prepared which were then melted a
- 15 second time at 1450 to 1550°C for 1 to 3 h for homogenization.

In the case of Examples 1 to 6 and 8 to 14, the obtained glass melts were then poured into preheated moulds in order to produce glass monoliths.

20

- In the case of Example 7, the obtained glass melt was cooled to 1400°C and converted to a fine-particle granular material by pouring into water. The granular material was dried and ground to a powder with a particle size of $< 90 \mu\text{m}$. This
- 25 powder was moistened with some water and pressed to form a powder green compact at a pressing pressure of 20 MPa.

- The glass monoliths (Examples 1-6 and 8-14) as well as the powder green compact (Example 7) were then converted by
- 30 thermal treatment to glasses and glass ceramics according to the invention. The thermal treatments used for controlled nucleation and controlled crystallization are also given in Table I. The following meanings apply

T_N and t_N	temperature and time used for nucleation
T_C and t_C	temperature and time used for crystallization of lithium disilicate or lithium metasilicate
LS	lithium metasilicate

It can be seen that a first heat treatment in the range of from 480 to 520°C resulted in the formation of lithium silicate glasses with nuclei and these glasses crystallized due to a further heat treatment already at 640 to 740°C to glass ceramics with lithium disilicate or lithium metasilicate as main crystal phase, as was established by X-ray diffraction tests.

15

The produced lithium silicate glass ceramics were able to be very satisfactorily machined into the form of various dental restorations, in a CAD/CAM process or by hot pressing, which restorations were also provided with a veneer if required.

20

They were also able to be applied by hot pressing as coatings onto in particular dental restorations, e.g. in order to veneer the latter as desired.

25 Example 15 - Processing via powder green compacts

The glass ceramics according to Examples 1 and 11 were ground to powders with an average particle size of < 90 µm.

30

In a first variant, the obtained powders were pressed with or without pressing auxiliaries to powder green compacts and the latter were partly or densely sintered at temperatures of from 800 to 1100°C and then further processed by machining or by hot pressing to form dental restorations.

35

In a second variant, the obtained powders were pressed with or without pressing auxiliaries to powder green compacts and the

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latter were then further processed by machining or by hot pressing to form dental restorations. In particular, the dental restorations obtained after the machining were then densely sintered at temperatures of from 900 to 1100°C.

5

With both variants, in particular crowns, caps, partial crowns and inlays as well as coatings on dental ceramics and dental glass ceramics were prepared.

10

Example 16 - Hot pressing of glass with nuclei

A glass with the composition according to Example 7 was prepared by mixing corresponding raw materials in the form of oxides and carbonates for 30 min in a TurbulaTM 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 fine-particle granular glass material. This granular glass 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 nucleated at 500°C and stress-relieved.

The nucleated glass cylinders were then processed by hot pressing at a pressing temperature of 970°C and a pressing time of 6 min using an EP600 press furnace, Ivoclar Vivadent AG, to form dental restorations, such as inlays, onlays, veneers, partial crowns, crowns, laminating materials and laminates. In each case, lithium disilicate was detected as main crystal phase.

Table I

Example	1	2	3	4	5	6	7
Composition	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%
SiO ₂	73.8	69.4	76.4	73.7	73.8	78.4	78.1
Li ₂ O	15.3	19.7	12.7	15.3	15.3	16.3	16.3
P ₂ O ₅	3.4	3.4	3.4	7.0	0.5	3.3	-
Al ₂ O ₃	-	-	-	-	-	-	-
ZrO ₂	3.5	3.5	3.5	2.0	5.2	-	-
TiO ₂	4.0	4.0	4.0	2.0	5.2	-	5.6
CeO ₂	-	-	-	-	-	2.0	-
GeO ₂	-	-	-	-	-	-	-
SnO ₂	-	-	-	-	-	-	-
Rb ₂ O	-	-	-	-	-	-	-
Cs ₂ O	-	-	-	-	-	-	-
CaO	-	-	-	-	-	-	-
Ag ₂ O	-	-	-	-	-	-	-
Pd	-	-	-	-	-	-	-
Au	-	-	-	-	-	-	-
SiO ₂ /Li ₂ O molar ratio	2.39	1.75	3.00	2.39	2.39	2.39	2.39
Optical properties (after pouring)	opaque glass	transparent	transparent	transparent	transparent	transparent	transparent
T _g /°C	489	482	495	479	503	483	483
T _N /°C	510	500	510	500	520	500	500
t _N /min.	10	10	10	10	10	10	10
T _C /°C	680	700	700	740	680	650	680
t _C /min.	20	20	20	20	20	20	40
Main crystal phase ^{RT-XRD}	lithium disilicate	lithium disilicate	lithium disilicate	lithium disilicate	lithium disilicate	lithium disilicate	lithium metasilicate
Other crystal phases	Li ₂ SiO ₃ , cristobalite	Li ₂ SiO ₃ , Li ₃ PO ₄	Li ₃ PO ₄	Li ₂ SiO ₃ , Li ₃ PO ₄	LS	-	-

Example	8	9	10	11	12	13	14
Composition	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%
SiO ₂	75.75	75.75	58.8	72.8	78.4	70.2	73.9
Li ₂ O	15.8	15.8	15.3	15.1	16.3	14.5	15.3
P ₂ O ₅	-	-	3.4	3.6	3.3	3.2	3.3
Al ₂ O ₃	3.0	3.0	3.0	-	-	2.9	-
ZrO ₂	5.4	5.4	-	2.5	-	5.0	-
TiO ₂	-	-	-	-	-	-	3.0
CeO ₂	-	-	-	-	-	-	-
GeO ₂	-	-	15.0	-	-	-	-
SnO ₂	-	-	-	-	2.0	-	-
Rb ₂ O	-	-	-	2.0	-	4.3	-
Cs ₂ O	-	-	4.5	-	-	-	4.5
CaO	-	-	-	3.8	-	-	-
Ag ₂ O	-	-	-	0.2	-	-	-
Pd	0.05	-	-	-	-	-	-
Au	-	0.05	-	-	-	-	-
SiO ₂ /Li ₂ O molar ratio	2.39	2.39	1.94	2.40	2.40	2.40	2.40
Optical properties (after pouring)	transparent	opaque glass	transparent	transparent	opaque glass	transparent	transparent
T _g /°C	489	486	459	462	472	485	479
T _N /°C	510	510	480	490	490	500	500
t _N /min.	10	10	10	10	10	10	10
T _C /°C	620	620	640	700	640	700	700
t _C /min.	30	30	30	20	20	20	20
Main crystal phase	lithium metasilicate	lithium metasilicate	lithium metasilicate	lithium disilicate	lithium disilicate	lithium disilicate	lithium disilicate
Other crystal phases	-	-	-	Li ₃ PO ₄	Li ₃ PO ₄	Li ₃ PO ₄	Li ₃ PO ₄

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CLAIMS:

1. Lithium silicate glass ceramic which comprises
tetraivalent metal oxide selected from ZrO_2 , TiO_2 ,
 CeO_2 , GeO_2 , SnO_2 and mixtures thereof,
5 67.0 to 79.0 wt.-% SiO_2 ,
at least 12.1 wt.-% Li_2O ,
0 to 6.0 wt.-% Al_2O_3 ,
less than 0.1 wt.-% La_2O_3 ,
less than 1.0 wt.-% K_2O and
10 less than 2.0 wt.-% Na_2O .
2. Glass ceramic according to claim 1, which comprises
less than 6.1 wt.-% ZrO_2 .
3. Glass ceramic according to claim 1 or 2, which further
comprises less than 8.5 wt.-% transition metal oxide selected
15 from the group consisting of oxides of yttrium, oxides of
transition metals with an atomic number from 41 to 79 and
mixtures of these oxides.
4. Glass ceramic according to any one of claims 1 to 3,
which comprises less than 0.5 wt.-% K_2O .
- 20 5. Glass ceramic according to claim 4, which comprises
less than 0.1 wt.-% K_2O .
6. Glass ceramic according to claim 5, which is
substantially free from K_2O .

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7. Glass ceramic according to any one of claims 1 to 6, which comprises less than 1.0 wt.-% Na₂O.

8. Glass ceramic according to claim 7, which comprises less than 0.5 wt.-% Na₂O.

5 9. Glass ceramic according to claim 8, which comprises less than 0.1 wt.-% Na₂O.

10. Glass ceramic according to claim 9, which is substantially free from Na₂O.

11. Glass ceramic according to any one of claims 1 to 10,
10 which is substantially free from La₂O₃.

12. Glass ceramic according to any one of claims 1 to 11, which comprises the tetravalent metal oxide or mixtures thereof in an amount of from 0.1 to 15 wt.-%.

13. Glass ceramic according to claim 12, which comprises
15 the tetravalent metal oxide or mixtures thereof in an amount of from 2.0 to 15.0 wt.-%.

14. Glass ceramic according to claim 13, which comprises the tetravalent metal oxide or mixtures thereof in an amount of from 2.0 to 8.0 wt.-%.

20 15. Glass ceramic according to any one of claims 1 to 14, which has lithium metasilicate as a main crystal phase.

16. Glass ceramic according to claim 15, which has more than
5 vol.-% lithium metasilicate crystals.

17. Glass ceramic according to claim 16, which has more
25 than 10 vol.-% lithium metasilicate crystals.

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18. Glass ceramic according to claim 17, which has more than 15 vol.-% lithium metasilicate crystals.

19. Glass ceramic according to any one of claims 1 to 14, which has lithium disilicate as a main crystal phase.

5 20. Glass ceramic according to claim 19, which has more than 10 vol.-% lithium disilicate crystals.

21. Glass ceramic according to claim 20, which has more than 20 vol.-% lithium disilicate crystals.

10 22. Glass ceramic according to claim 21, which has more than 30 vol.-% lithium disilicate crystals.

23. Glass ceramic according to any one of claims 1 to 22, which comprises 12.5 to 20.0 wt.-% Li_2O .

24. Glass ceramic according to claim 23, which comprises 15.0 to 17.0 wt.-% Li_2O .

15 25. Glass ceramic according to any one of claims 1 to 24, which comprises 0 to 10.0 wt.-% P_2O_5 .

26. Glass ceramic according to claim 25, which comprises 0.5 to 9.0 wt.-% P_2O_5 .

20 27. Glass ceramic according to claim 26, which comprises 2.5 to 7.5 wt.-% P_2O_5 .

28. Glass ceramic according to any one of claims 1 to 11 and 15 to 22, which comprises at least one of the following components in the indicated amounts:

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<u>Component</u>	<u>wt.-%</u>
Li ₂ O	12.5 to 20.0

tetravalent metal

oxide or mixtures

5	thereof	2.0 to 15.0
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	P ₂ O ₅	0 to 7.0.
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29. Glass ceramic according to claim 28, wherein the amount of the P₂O₅ is from 0.5 to 7.0 wt.-%.

30. Glass ceramic according to claim 28 or 29, wherein
10 the amount of Al₂O₃ is from 0.5 to 3.5 wt.-%.

31. Glass ceramic according to any one of claims 28 to 30, which comprises all of the defined components in the indicated amounts.

32. Glass ceramic according to any one of claims 1 to 14
15 and 19 to 31, which has lithium disilicate as main crystal phase and a fracture toughness, measured as K_{IC} value, of at least 1.9 MPa•m^{0.5}.

33. Glass ceramic according to claim 32, wherein the glass ceramic has a fracture toughness, measured as K_{IC} value
20 of more than 2.3 MPa•m^{0.5}.

34. Glass ceramic according to any one of claims 1 to 33, which comprises SiO₂ and Li₂O in a molar ratio of from 1.7 to 3.1.

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35. Glass ceramic according to claim 34, wherein the molar ratio is from 1.75 to 3.0.

36. Glass ceramic according to any one claims 1-33, which comprises SiO_2 and Li_2O in a molar ratio of at least 2.2.

5 37. Glass ceramic according to claim 36, wherein the molar ratio is from 2.3 to 2.5.

38. Glass ceramic according to claim 37, wherein the molar ratio is about 2.4.

39. Starting glass, which comprises the components of the
10 glass ceramic according to any one of claims 1 to 14, 23 to 31, and 34 to 38.

40. Lithium silicate glass with nuclei which are for forming lithium metasilicate and/or lithium disilicate crystals, wherein the glass comprises the components of the glass ceramic
15 according to any one of claims 1 to 14, 23 to 31, and 34 to 38.

41. Glass ceramic according to any one of claims 1 to 33 or glass according to claim 39 or 40, wherein the glass or the glass ceramic is present in the form of a powder, a granular material, a blank or a dental restoration.

20 42. Process for the preparation of the glass ceramic according to any one of claims 1 to 33 and 41 or of the glass according to claim 39 or 41, wherein the starting glass according to claim 39 or 41, the glass with nuclei according to claim 40 or 41 or the glass ceramic with lithium metasilicate
25 as main crystal phase according to any one of claims 15 to 18,

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23 to 31, 34 to 38 and 41 is subjected to at least one heat treatment in the range of from 450 to 950°C.

43. Process according to claim 42, wherein the heat treatment is in the range of from 450 to 750°C.

5 44. Process according to claim 43, wherein the heat treatment is in the range of 480 to 740°C.

45. Process for the preparation of a lithium silicate glass ceramic which comprises

10 tetraivalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof,

at least 12.1 wt.-% Li_2O ,

less than 0.1 wt.-% La_2O_3 ,

less than 1.0 wt.-% K_2O and

less than 2.0 wt.-% Na_2O ,

15 wherein

(a) a starting glass which comprises the components of the glass ceramic is subjected to a heat treatment at a temperature of from 480 to 520°C for a period of from 10 min to 120 min in order to form a glass with nuclei which are suitable for
20 forming lithium disilicate crystals, and

(b) the glass with nuclei is subjected to a heat treatment at a temperature of from 640 to 740°C in order to form a glass ceramic with lithium disilicate as a main crystal phase.

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46. Use of a glass ceramic, a starting glass, or a glass with nuclei which are suitable for forming lithium metasilicate and/or lithium disilicate crystals, wherein the glass ceramic or the glass comprises

5 tetraivalent metal oxide selected from ZrO_2 , TiO_2 , CeO_2 , GeO_2 , SnO_2 and mixtures thereof,

67.0 to 79.0 wt.-% SiO_2 ,

at least 12.1 wt.-% Li_2O ,

less than 0.1 wt.-% La_2O_3 ,

10 less than 1.0 wt.-% K_2O and

less than 2.0 wt.-% Na_2O ,

as dental material.

47. The use of claim 46, wherein the dental material is for coating dental restorations.

15 48. The use of claim 46, wherein the dental material is for the preparation of dental restorations.

49. Use for the preparation of dental restorations according to claim 48, wherein the glass ceramic or the glass is shaped by pressing or machining to the dental restoration.

20 50. The use of claim 49, wherein the dental restoration is a bridge, inlay, onlay, veneer, partial crown, crown, facet or abutment.