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(72) Inventeurs/Inventors:
RHEINBERGER, VOLKER, LI;
RAMPF, MARKUS, CH;
DITTMER, MARC, AT;
RITZBERGER, CHRISTIAN, CH;
HOLAND, WOLFRAM, LI;
SCHWEIGER, MARCEL, CH

(73) Propriétaire/Owner:
IVOCLAR VIVADENT AG, LI

(74) Agent: SMART & BIGGAR

(54) Titre : VITROCERAMIQUE DE SILICATE DE LITHIUM ET VERRE PRESENTANT UNE TENEUR EN OXYDE DE RUBIDIUM
(54) Title: LITHIUM SILICATE GLASS CERAMIC AND GLASS WITH RUBIDIUM OXIDE CONTENT

(57) Abrégé/Abstract:
The invention relates to the use of lithium silicate glass ceramics and glasses with rubidium oxide content for coating an oxide ceramic, a metal or an alloy.

Abstract

The invention relates to the use of lithium silicate glass ceramics and glasses with rubidium oxide content for coating an oxide ceramic, a metal or an alloy.

Lithium silicate glass ceramic and glass with rubidium oxide content

The invention relates to lithium silicate glass ceramic and lithium silicate glass which comprise rubidium oxide and are characterized by a linear coefficient of thermal expansion that is adjustable in a broad range of in particular 9.0 to $14.0 \cdot 10^{-6}$ K^{-1} and are therefore suitable primarily in the dental field for veneering oxide ceramic restorations and metal restorations.

In dentistry, dental restorations are usually veneered with ceramic layers in order to match the appearance of the restoration to that of the natural teeth. Such veneered restorations are also called veneer ceramics. In order to avoid stresses between the restoration material to be veneered and the ceramic layer, it is necessary for the coefficients of thermal expansion of the ceramic materials to be adapted to that of the restoration material.

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 translucence and very good mechanical properties, are used in particular in the dental field and primarily for producing dental crowns and small bridges. The known lithium silicate glass ceramics usually contain as main components SiO_2, Li_2O, Al_2O_3, Na_2O or K_2O, and nucleating agents such as P_2O_5.

EP 0 885 855 A2 and EP 0 885 856 A2 describe apatite-containing glass ceramics with excellent optical and chemical properties and a strength in the region of 110 MPa, which are suitable for veneering ZrO_2 frameworks.

WO 2004/021921 A1 describes a glass for veneering ZrO_2, but which only has a low strength.

EP 1 253 116 A1 describes a mixture of a lithium silicate glass with leucite crystals for veneering metal frameworks. This glass also has only an inadequate strength.

WO 2012/082156 A1 describes a lithium silicate product for veneering metal frameworks with a coefficient of expansion $CTE_{100-400°C}$ of from 12 to $13.5 \cdot 10^{-6}\ K^{-1}$ and strengths of up to 300 MPa.

EP 2 377 831 A1 describes a lithium silicate glass ceramic with ZrO_2 content. The coefficient of expansion of the glass ceramic is not suitable for veneering metal frameworks.

In order for a dental glass ceramic to be able to be used for veneering the whole spectrum of the customarily used restoration materials, such as from dental metals and alloys to oxide ceramics, it is necessary for its coefficient of expansion to be adjustable in a broad range. Moreover, the glass ceramics must satisfy high requirements with regard to their optical and mechanical properties and in particular must have a very high strength.

Known glass ceramics and glasses often do not satisfy the requirement for coefficients of thermal expansion that are adjustable in a broad range and for adequate strength. Further, with the known glass ceramics the alkaline earth metal oxide BaO as well as the alkali metal oxides K_2O and/or Na_2O are as a rule present as essential components which are clearly required there for the production of the glass ceramics and in particular the formation of the usually sought lithium disilicate main crystal phase.

There is therefore a need for lithium silicate glass ceramics in which the linear coefficient of thermal expansion $CTE_{100-400°C}$ is adjustable over a broad range and in particular in the range of from 9.0 to $14.0 \cdot 10^{-6}$ K^{-1} and preferably in the range of from 9.6 to $12.8 \cdot 10^{-6}$ K^{-1}. Further, they should also be able to be produced without the alkali metal oxides K_2O or Na_2O, previously regarded as necessary, as well as in particular without the alkaline earth metal oxide BaO, and be suitable in particular for veneering dental restorations, including oxide ceramic restorations and metal restorations, primarily on the basis of their optical and mechanical properties.

This object is achieved by the use of a lithium silicate glass ceramic or a lithium silicate glass as described herein.
A subject of the invention is likewise the method as described herein, the composite material as described herein, the lithium silicate glass ceramic as described herein and the lithium silicate glass as described herein.

The use according to the invention is characterized in that a lithium silicate glass ceramic or a lithium silicate glass which comprises the following components

Component	wt.-%
SiO_2	56.0 to 73.0
Li_2O	13.0 to 19.0
Rb_2O	3.0 to 9.0
Al_2O_3	2.0 to 5.0
P_2O_5	2.0 to 6.0

is used for coating a substrate selected from oxide ceramics, metals and alloys.

It has surprisingly been shown that the lithium silicate glass ceramic according to the invention has a linear coefficient of thermal expansion $CTE_{100-400^{\circ}C}$ which is easily adjustable in a broad range of in particular 9.0 to $14.0 \cdot 10^{-6}$ K^{-1} and preferably 9.6 to $12.8 \cdot 10^{-6}$ K^{-1}, and moreover has excellent optical and mechanical properties such as high strength and fracture toughness. This glass ceramic is therefore suitable for coating both oxide ceramics as well as metals and alloys. It is particularly surprising that the formation of a glass ceramic with lithium meta- and/or disilicate as main crystal phase is successful even in the absence of various components regarded as necessary for conventional glass ceramics, such as in particular K_2O, Na_2O and BaO. The formation of the glass ceramic according to the invention can also be achieved by the use of the lithium silicate glass according to the invention, which represents a precursor for the lithium silicate glass ceramic and can be converted to same before, during or after the application to the substrate.

It is preferred that the lithium silicate glass ceramic used according to the invention and the lithium silicate glass used according to the invention comprise at least one and preferably all of the following components in the given amounts

Component	wt.-%
SiO_2	56.9 to 72.0
Li_2O	14.2 to 18.0
Rb_2O	3.7 to 7.7
Al_2O_3	2.5 to 4.5
P_2O_5	3.1 to 5.0
ZrO_2	0 to 4.5, in particular 0 to 4.0
Transition metal oxide	0 to 7.5, in particular 0 to 7.0,

wherein the transition metal oxide is selected 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.

The lithium silicate glass ceramic and the lithium silicate glass preferably comprise 58.0 to 72.0, in particular 60.0 to 71.0 and preferably 63.0 to 70.0 wt.-% SiO_2.

It is also preferred that the lithium silicate glass ceramic and the lithium silicate glass comprise 14.4 to 17.5, in particular 14.5 to 17.0 and particularly preferably 14.8 to 16.0 wt.-% Li_2O.

In a preferred embodiment, the molar ratio of SiO_2 to Li_2O is from 2.0 to 3.0, in particular from 2.2 to 2.6, preferably from 2.3 to 2.5 and particularly preferably about 2.4. In another preferred embodiment, the molar ratio of SiO_2 to Li_2O is less than 2.0, in particular from 1.5 to 1.9, preferably from 1.6 to 1.8 and particularly preferably about 1.7.

It is preferred that the lithium silicate glass ceramic and the lithium silicate glass comprise 3.7 to 7.7 wt.-%, in particular 5.1 to 7.7 wt.-% and preferably 6.1 to 7.4 wt.-% Rb_2O.

It is also preferred that the lithium silicate glass ceramic and the lithium silicate glass comprise 2.5 to 4.0 wt.-%, in particular 3.0 to 3.5 wt.-% and preferably 3.2 to 3.4 wt.-% Al_2O_3.

The molar ratio of Rb_2O to Al_2O_3 is preferably at least 0.1, in particular from 0.2 to 2.0, preferably from 0.25 to 1.25 and particularly preferably from 0.5 to 1.0.

The glass and the glass ceramic preferably comprise 3.2 to 4.5 wt.-% and in particular 3.4 to 4.0 wt.-% P_2O_5 as nucleating agent.

The lithium silicate glass ceramic used according to the invention and the lithium silicate glass used according to the invention can moreover also comprise additional components which are selected in particular from further oxides of monovalent elements, oxides of divalent elements, further oxides of trivalent elements, further oxides of tetravalent elements, further oxides of pentavalent elements, oxides of hexavalent elements, melt accelerators, colorants and fluorescent agents. In a preferred embodiment, the lithium silicate glass ceramic and the lithium silicate glass comprise additional components in an amount of from 0 to 20.0 wt.-%, in particular 0.1 to 10.0 wt.-%, preferably 0.5 to 7.5 wt.-% and most preferably 1.0 to 5.0 wt.-%.

The term "further oxides of monovalent elements" refers to oxides of monovalent elements and in particular alkali metal oxides with the exception of Li_2O and Rb_2O. Examples of suitable further oxides of monovalent elements are Na_2O, K_2O, Cs_2O and mixtures thereof and in particular Na_2O, K_2O and mixtures thereof.

In an embodiment, the lithium silicate glass ceramic and the lithium silicate glass comprise 0.1 to 2.0 wt.-%, in particular

0.2 to 1.5 wt.-%, preferably 0.3 to 1.4 wt.-% and particularly preferably 0.5 to 1.0 wt.-% Na_2O. In a further embodiment, the lithium silicate glass ceramic and the lithium silicate glass comprise 0.1 to 2.0 wt.-%, in particular 0.2 to 1.6 wt.-%, preferably 0.4 to 1.5 wt.-% and particularly preferably 0.5 to 1.0 wt.-% K_2O. In a particularly preferred embodiment, the lithium silicate glass ceramic and the lithium silicate glass comprise less than 4.0 wt.-%, in particular less than 3.5 wt.-%, preferably less than 3.0 wt.-%, particularly preferably less than 2.5 wt.-% and most preferably less than 2.0 wt.-% Na_2O and/or K_2O.

The lithium silicate glass ceramic and the lithium silicate glass preferably comprise less than 2.5 wt.-%, in particular less than 1.5 wt.-%, preferably less than 1.0 wt.-%, particularly preferably less than 0.5 wt.-% Cs_2O. They are most preferably substantially free of Cs_2O.

In particular the alkaline earth metal oxides, preferably MgO, CaO, SrO, BaO and mixtures thereof, and preferably CaO, SrO and mixtures thereof, come into consideration as oxides of divalent elements.

The lithium silicate glass ceramic and the lithium silicate glass preferably comprise less than 3.8 wt.-%, in particular less than 2.5 wt.-%, preferably less than 1.5 wt.-%, particularly preferably less than 0.5 wt.-% BaO. They are most preferably substantially free of BaO.

The term "further oxides of trivalent elements" refers to oxides of trivalent elements with the exception of Al_2O_3. Suitable oxides of trivalent elements are in particular Y_2O_3, La_2O_3, Bi_2O_3 and mixtures thereof, and preferably Y_2O_3 and La_2O_3.

The term "further oxides of tetravalent elements" refers to oxides of tetravalent elements with the exception of SiO_2.

Examples of suitable further oxides of tetravalent elements are TiO_2, GeO_2 and ZrO_2.

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 are Ta_2O_5 and Nb_2O_5.

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

A glass and a glass ceramic which comprise at least one further oxide of monovalent elements, one oxide of divalent elements, at least one further oxide of trivalent elements, at least one further oxide of tetravalent elements, at least one further oxide of pentavalent elements and/or at least one oxide of hexavalent elements are preferred.

Examples of melt accelerators are fluorides.

Examples of colorants and fluorescent agents are oxides of d- 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 colorants and in addition can also act as nucleating agents. These metal colloids can be formed e.g. by reduction of corresponding oxides, chlorides or nitrates during the melting and crystallization processes. The metal colloids are preferably present in the glass ceramic in an amount of from 0.005 to 0.5 wt.-%.

The glass ceramic used according to the invention preferably has lithium metasilicate and/or lithium disilicate as main crystal phase. The term "main crystal phase" denotes the crystal phase which has the highest proportion by volume compared with the other crystal phases. If two crystal phases have approximately the same proportion by volume, these crystal phases can both be present as main crystal phases. In other embodiments, lithium metasilicate can be present as main crystal phase and lithium disilicate as secondary phase or lithium disilicate as main crystal phase and lithium metasilicate as secondary phase.

It has surprisingly been shown that the lithium silicate glass ceramic according to the invention has very good mechanical and optical properties even in the absence of components regarded as necessary for conventional glass ceramics. The combination of their properties even allows them to be used as dental material and in particular for coating dental restorations.

The lithium silicate glass ceramic according to the invention preferably has a fracture toughness, measured as K_{IC} value, of at least about 2.0 $MPa \cdot m^{0.5}$ and in particular at least about 2.3 $MPa \cdot m^{0.5}$. This value was determined using the Vickers method and calculated using Niihara's equation. Further, it has a high biaxial breaking strength of preferably 180 to 700 MPa. Moreover, it displays a high chemical stability ascertained by mass loss after storage in acetic acid. The chemical stability is in particular less than 100 $\mu g/cm^2$. The biaxial breaking strength and the chemical stability were determined according to ISO 6872 (2008).

In a preferred embodiment, the glass ceramic comprises lithium metasilicate as main crystal phase. In particular the glass ceramic comprises more than 5 vol.-%, preferably more than 10 vol.-% and particularly preferably more than 15 vol.-% lithium metasilicate crystals, relative to the total glass ceramic. This lithium metasilicate glass ceramic is characterized by very good mechanical properties. It preferably has a bending strength in the range of about 180 to 300 MPa and/or a fracture toughness, measured as K_{IC} value, of at least about 2.0 $MPa \cdot m^{0.5}$ and in particular at least about 2.3 $MPa \cdot m^{0.5}$. It can be formed e.g. by heat treatment of a corresponding lithium silicate glass and in particular of a corresponding lithium silicate glass with nuclei.

In a further particularly preferred embodiment, the glass ceramic 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.-% lithium disilicate crystals, relative to the total glass ceramic. This lithium disilicate glass ceramic is characterized by particularly good mechanical properties. It preferably has a bending strength in the range of about 400 to 700 MPa and/or a fracture toughness, measured as K_{IC} value, of at least about 2.0 $MPa \cdot m^{0.5}$ and in particular at least about 2.3 $MPa \cdot m^{0.5}$. It can be produced e.g. by heat treatment of the lithium metasilicate glass ceramic. However, it can also be formed by heat treatment of a corresponding lithium silicate glass or a corresponding lithium silicate glass with nuclei.

In particular Li_3PO_4, SiO_2 and TiO_2 come into question as further crystal phases of the lithium silicate glass ceramic.

In a further embodiment, a lithium silicate glass is used. This lithium silicate glass preferably comprises nuclei which are suitable for the formation of lithium metasilicate and/or lithium disilicate crystals. Such a lithium silicate glass with nuclei can be formed in particular by heat treatment of a corresponding lithium silicate glass. The lithium metasilicate glass ceramic according to the invention can then be formed by a further heat treatment, and in turn be converted to 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. Consequently, the lithium silicate glass, the lithium silicate glass with nuclei and the lithium metasilicate glass ceramic can be regarded as precursors for producing a high-strength lithium meta- or disilicate glass ceramic according to the invention. The lithium silicate glass is preferably converted to a glass ceramic as described above before, during or after application to the substrate.

To produce the lithium silicate glass, the procedure can be in particular that a mixture of suitable starting materials, such as carbonates, oxides, phosphates and fluorides, is melted at temperatures of in particular 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 lithium silicate glass, so-called solid glass blanks or monolithic blanks. It is also possible to put the melt into water again in order to produce a granulate. This granulate can then be pressed, after grinding and optionally addition of further components, such as colorants and fluorescent agents, to form a blank, a so-called powder green compact. Finally, the lithium silicate glass can also be processed to form a powder after granulation.

The lithium silicate 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 1050°C. It is preferred that a first heat treatment is initially carried out at a temperature in the range of from 480 to 580°C, in particular 480 to 560°C and preferably 480 to 520°C to produce a glass 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 5 to 120 minutes, in particular 10 to 60 minutes and preferably 10 to 30 minutes. The glass with nuclei can then preferably be subjected to at least one further temperature treatment at a higher temperature and in particular more than 580°C to effect crystallization of lithium metasilicate or lithium disilicate. This further heat treatment is preferably carried out for a period of from 10 to 120 minutes, in particular 10 to 60 minutes and particularly preferably 20 to 30 minutes. To crystallize lithium metasilicate, the further heat treatment is usually carried out at 600 to 950°C, preferably 620 to 850°C and quite particularly preferably 650 to 750°C. To crystallize lithium disilicate, the further heat treatment is usually carried out at 750 to 1050°C, preferably 800 to 1000°C, particularly preferably 820 to 950°C and quite particularly preferably 850 to 900°C.

The lithium silicate glass ceramic used according to the invention and the lithium silicate glass used according to the invention are present in particular in the form of powders, granulates or blanks, e.g. monolithic blanks, such as discs, cuboids or cylinders, or powder green compacts, in unsintered, partly sintered or densely-sintered form. They can easily be further processed in these forms. However, they can also be present in the form of an overstructure for dental restorations, such as in particular crowns. It is preferred that the glass ceramic or the glass is shaped into the desired geometry by machining or pressing.

The lithium silicate glass ceramic used according to the invention and the lithium silicate glass used according to the invention are suitable in particular for coating oxide ceramics, metals and alloys.

In a preferred embodiment, the substrate is an oxide ceramic. Zirconium oxide ceramics are particularly preferred. Examples of suitable zirconium oxide ceramics are ceramics based on polycrystalline tetragonal zirconium oxide (tetragonal zirconia polycrystal, TZP) in which the tetragonal form is stabilized by the addition of Y_2O_3 and/or CeO_2.

In another preferred embodiment, the substrate is a metal or an alloy. Non-precious metal alloys and in particular non-ferrous alloys which are suitable for dental applications are particularly preferred. Examples of suitable alloys are in particular alloys of the Ni-Cr, Co-Cr and Co-Cr-W type.

It is furthermore preferred that the substrate is a dental restoration and in particular a bridge, an inlay, an onlay, a veneer, an abutment, a partial crown, a crown or a facet.

The invention also relates to a process for coating a substrate selected from oxide ceramics, metals and alloys, in which a lithium silicate glass ceramic as described above or a lithium silicate glass as described above are applied to the substrate. The substrate is preferably a preferred substrate as described above.

In an embodiment of the process according to the invention, the lithium silicate glass ceramic or the lithium silicate glass is applied to the substrate by sintering and preferably by pressing-on.

During sintering, the lithium silicate glass ceramic according to the invention or the lithium silicate glass according to the invention is applied in customary manner, e.g. as powder, to the material to be coated and then sintered at increased temperature.

During the preferred pressing-on, the lithium silicate glass ceramic according to the invention or the lithium silicate glass according to the invention, e.g. in the form of powder green compacts or monolithic blanks, is converted to a viscous state at an increased temperature of e.g. 700 to 1200°C and pressed onto the substrate using low pressure, e.g. 2 to 10 bar. For this, in particular the methods described in EP 231 773 A1 and the press furnace disclosed there can be used. A suitable furnace is e.g. the Programat EP 5000 from Ivoclar Vivadent AG.

In another embodiment of the process according to the invention, the lithium silicate glass ceramic or the lithium silicate glass is applied to the substrate by joining. Suitable joining methods are known per se and comprise for example joining by means of a glass or glass ceramic solder, joining by adhesion by means of an adhesive or dental cement, joining by sagging by means of a temperature treatment in which the materials to be joined are softened, and joining by friction welding or wringing.

In a particularly preferred embodiment, the lithium silicate glass ceramic or the lithium silicate glass is shaped to a desired geometry by hot pressing or by machining before joining.

The hot pressing is usually carried out at increased pressure and increased temperature. It is preferred that the hot pressing is carried out at a temperature of from 700 to 1200°C. It is further preferred to carry out the hot pressing at a pressure of from 2 to 10 bar. The desired shape change is achieved by viscous flow of the material used. The lithium metasilicate glass ceramic according to the invention, the lithium disilicate glass ceramic according to the invention, the lithium silicate glass according to the invention and in particular the lithium silicate glass with nuclei according to the invention can be used for the hot pressing. The glass ceramics and glasses 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 machining is usually carried out by material removal 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. For the machining, the lithium silicate glass, the lithium silicate glass with nuclei, the lithium metasilicate and lithium disilicate glass ceramic can be used. The glasses and glass ceramics 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. For the machining, lithium silicate glass ceramic in particular with lithium disilicate and preferably with lithium metasilicate as main crystal phase is preferably used. The lithium silicate 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 750 to 1050°C, preferably 800 to 950°C and particularly preferably about 850 to 900°C in order to effect further crystallization of lithium metasilicate or preferably lithium disilicate.

In general, the lithium silicate glass ceramic or the lithium silicate glass can also in particular be heat-treated after the shaping by hot pressing or machining, in order to convert precursors used, such as lithium silicate glass, lithium silicate glass with nuclei or lithium metasilicate glass ceramic, to lithium meta- and/or disilicate glass ceramic, increase the crystallization of lithium meta- and/or disilicate, or reduce the porosity e.g. of a porous powder green compact used.

It is preferred that, after the coating procedure has been completed, a coating is obtained which comprises a lithium silicate glass ceramic with lithium meta- and/or disilicate as main crystal phase as it has particularly good properties. Glass ceramics which have the crystal phases and mechanical properties described above are particularly preferred.

Furthermore, the invention relates to a composite material which comprises a lithium silicate glass ceramic as defined above or a lithium silicate glass as defined above on a substrate selected from oxide ceramics, metals and alloys. All embodiments are preferred which are also given as preferred for the lithium silicate glass ceramic used according to the invention, the lithium silicate glass used according to the invention as well as the substrate. The composite material can be produced in particular by means of the process according to the invention.

The invention also relates to a lithium silicate glass ceramic which comprises the following components

Component	wt.-%
SiO_2	56.0 to 72.5, in particular 56.9 to 72.0
Li_2O	13.0 to 19.0, in particular 14.2 to 18.0
Rb_2O	3.0 to 9.0, in particular 3.7 to 7.7
Al_2O_3	2.0 to 5.0, in particular 2.5 to 4.5
P_2O_5	2.0 to 6.0, in particular 3.1 to 5.0
ZrO_2	0 to 4.5, in particular 0 to 4.0
Transition metal oxide	0 to 7.5, in particular 0 to 7.0,

wherein the transition metal oxide is selected 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.

Moreover, the invention also relates to a lithium silicate glass which comprises the components of the above glass ceramic.

In addition, the lithium silicate glass and the lithium silicate glass ceramic can also comprise still further components such as are given above for the lithium silicate glass ceramic used according to the invention and the lithium silicate glass used according to the invention. All embodiments are preferred which are also given as preferred for the lithium silicate glass ceramic used according to the invention and the lithium silicate glass used according to the invention.

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

Examples

A total of 15 glasses and glass ceramics according to the invention with the compositions given in Table I were produced by melting corresponding starting glasses followed by heat treatment for controlled nucleation and crystallization.

For this, the starting glasses in an amount of 100 to 200 g were first melted from customary raw materials at 1450 to 1550°C, wherein the melting was very easily possible without formation of bubbles or streaks. By pouring the starting glasses into water, glass frits were produced which were then melted a second time at 1450 to 1550°C for 1 to 3 h for homogenization. The obtained glass melts were then poured into pre-heated moulds to produce glass monoliths. All glass monoliths proved transparent.

The glass monoliths were then converted to glasses and glass ceramics according to the invention by thermal treatment. 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 first crystallization
T_{FC} and t_{FC}	Temperature and time used for final crystallization

T_{press} and t_{press} Temperature and time used for hot pressing

It can be seen that a first heat treatment in the range of from 470 to 500°C resulted in the formation of lithium silicate glasses with nuclei and these glasses crystallized as a result of further heat treatment at 600 to 710°C (Examples 1-6, 8-9 and 13) to form glass ceramics with lithium metasilicate as main crystal phase or as a result of heat treatment at 880°C (Examples 7 and 14) directly to form glass ceramics with lithium disilicate as main crystal phase, as was established by X-ray diffraction tests. A final heat treatment at a temperature of from 860 to 950°C (Examples 1, 3-4, 6-8, 10-12 and 14) finally resulted in the formation of glass ceramics with lithium disilicate as main crystal phase. By contrast, a final heat treatment at a temperature of only 820 to 840°C (Examples 2, 5, 9 and 13) resulted in the formation of glass ceramics with lithium metasilicate as main crystal phase.

The produced lithium disilicate glass ceramics had high fracture toughness values, measured as critical stress intensity factor K_{IC} according to the SEVNB method, of more than 2 $MPa\cdot m^{0.5}$ and in particular even at least 2.3 $MPa\cdot m^{0.5}$.

The biaxial strength σ_B was also high, at more than 400 MPa and up to more than 600 MPa. It was determined according to dental standard ISO 6872 (2008) on test pieces that were produced by machining of the respective lithium disilicate glass ceramic. A CEREC-InLab machine (Sirona, Bensheim) was used for the processing.

They were also able to be applied by hot pressing as coatings in particular onto oxide ceramic restorations or metal restorations, e.g. in order to veneer them as desired.

Table I

Example	1	2	3	4	5	6	7	8	9	10
Composition	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%
SiO_2	70.9	59.9	72.0	70.0	56.9	69.1	68.9	69.4	57.1	70.0
Li_2O	14.8	18.0	15.0	14.5	15.5	14.4	14.9	14.5	16.0	14.5
Rb_2O	7.7	7.7	6.3	6.1	7.7	6.0	3.7	6.1	7.7	6.1
Al_2O_3	3.4	3.5	3.4	3.2	3.4	3.3	3.0	3.2	3.5	3.2
P_2O_5	3.2	3.4	3.3	3.3	3.3	3.1	4.0	3.3	5.0	3.3
Na_2O	-	-	-	-	-	-	-	-	-	-
K_2O	-	-	-	-	-	-	1.4	-	-	-
Cs_2O	-	-	-	-	-	-	-	-	-	-
MgO	-	-	-	-	0.3	0.3	-	-	-	-
CaO	-	-	-	-	-	-	-	-	3.0	-
Y_2O_3	-	-	-	-	-	-	-	-	-	-
La_2O_3	-	-	-	-	-	-	-	-	1.5	-
GeO_2	-	-	-	-	8.0	-	-	-	0.8	-
ZrO_2	-	5.0	-	0.4	2.0	0.9	1.4	0.8	2.0	0.4
CeO_2	-	2.0	-	1.8	2.0	2.0	1.8	1.9	2.0	1.8
V_2O_5	-	0.1	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Tb_4O_7	-	0.3	-	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Er_2O_3	-	0.1	-	0.1	0.3	0.3	0.3	0.2	0.3	0.1
F	-	-	-	-	-	-	-	-	0.5	-

Example	1	2	3	4	5	6	7	8	9	10
T_g / °C	471	476	468	468	465	471	467	477	447	468
T_N / °C	490	500	490	490	480	490	500	500	470	490
t_N / min	10	30	10	10	10	10	10	10	10	10
T_C / °C	700	700	700	700	620	710	880	700	660	
t_C / min	20	20	20	20	40	20	30	20	30	
Main crystal phase	Li_2SiO_3	Li_2SiO_3	Li_2SiO_3	Li_2SiO_3	Li_2SiO_3	Li_2SiO_3	$Li_2Si_2O_5$	Li_2SiO_3	Li_2SiO_3	
Other crystal phases			$Li_2Si_2O_5$	$Li_2Si_2O_5$		$Li_2Si_2O_5$	Li_3PO_4	$Li_2Si_2O_5$		
T_{FC} / °C	880	820	880	870	830	860		870	820	
t_{FC} / min	7	20	7	7	7	7		7	10	
T_{press} / °C							950			930
t_{Press} / min							25			25
Main crystal phase	$Li_2Si_2O_5$	Li_2SiO_3	$Li_2Si_2O_5$	$Li_2Si_2O_5$	Li_2SiO_3	$Li_2Si_2O_5$	$Li_2Si_2O_5$	$Li_2Si_2O_5$	Li_2SiO_3	$Li_2Si_2O_5$
Other crystal phases	Li_2SiO_3 Li_3PO_4	Li_3PO_4	Li_3PO_4	Li_3PO_4	$Li_2Si_2O_5$ Li_3PO_4	Li_3PO_4	Li_3PO_4	Li_3PO_4	Li_3PO_4 $Ca_5(PO_4)_3F$	Li_3PO_4
L*				76.50		71.90	79.11	73.26		
a*				3.37		9.34	6.32	8.40		
b*				20.96		25.32	31.80	26.42		
CR				89.85		84.79	68.55	84.29		
$CTE_{100-400°C}$ / $10^{-6} \cdot K^{-1}$		12.8	9.70		11.7		9.70		12.0	
K_{IC} / MPa $m^{0.5}$										
σ_B / MPa	687		576							

L*,a*,b*: colour coordinates of the samples, determined according to DIN 5033 and DIN 6174

Example	11	12	13	14	15
Composition	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%
SiO_2	69.1	69.4	63.3	68.6	69.5
Li_2O	14.4	14.5	18.0	14.2	14.4
Rb_2O	6.0	6.1	7.7	7.4	5.4
Al_2O_3	3.3	3.2	3.5	2.5	4.5
P_2O_5	3.1	3.3	3.4	3.4	3.4
Na_2O	-	-	-	-	-
K_2O	-	-	-	-	-
Cs_2O	-			-	1.0
MgO	0.3	-	-	-	-
CaO	-	-	-	-	-
Y_2O_3	-	-	3.0	-	-
La_2O_3	-	-	-	-	-
GeO_2	-	-	-	-	-
ZrO_2	0.9	0.8	-	1.5	1.8
CeO_2	2.0	1.9	1.0	1.7	-
V_2O_5	0.1	0.1	0.1	0.1	-
Tb_4O_7	0.5	0.5	-	0.5	-
Er_2O_3	0.3	0.2	-	0.1	-
F	-	-	-	-	-

Example	11	12	13	14	15
T_g / °C	471	477	460	480	
T_N / °C	490	500	480	500	
t_N / min	10	10	10	10	
T_C / °C			600	880	
t_C / min			60	30	
Main crystal phase			Li_2SiO_3	$Li_2Si_2O_5$	
Other crystal phases				Li_3PO_4	
T_{FC} / °C			840		
t_{FC} / min			10		
T_{press} / °C	940	930		950	
t_{Press} / min	25	25		25	
Main crystal phase	$Li_2Si_2O_5$	$Li_2Si_2O_5$	Li_2SiO_3	$Li_2Si_2O_5$	
Other crystal phases	Li_3PO_4	Li_3PO_4	Li_3PO_4	Li_3PO_4	
L*	71.18			81.27	
a*	10.29			2.93	
b*	32.91			24.26	
CR	75.60			69.77	
$CTE_{100-400°C}$ / $10^{-6} \cdot K^{-1}$			12.4	9.6	
K_{IC} / MPa $m^{0.5}$	2.30				
σ_B / MPa	411				

L*,a*,b*: colour coordinates of the samples, determined according to DIN 5033 and DIN 6174

CR: contrast value as a measure of the translucence, determined according to BS 5612

CLAIMS:

1. Use of a lithium silicate glass ceramic or a lithium silicate glass which comprise the following components

Component	wt.-%
SiO_2	56.0 to 73.0
Li_2O	13.0 to 19.0
Rb_2O	3.0 to 9.0
Al_2O_3	2.0 to 5.0
P_2O_5	2.0 to 6.0,

for coating a substrate selected from metals and alloys.

2. Use according to claim 1, in which the lithium silicate glass ceramic or the lithium silicate glass comprise at least one of the following components in the given amounts

Component	wt.-%
SiO_2	56.9 to 72.0
Li_2O	14.2 to 18.0
Rb_2O	3.7 to 7.7
Al_2O_3	2.5 to 4.5
P_2O_5	3.1 to 5.0
ZrO_2	0 to 4.5
Transition metal oxide	0 to 7.5,

wherein the transition metal oxide is selected 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.

3. Use according to claim 1, in which the lithium silicate glass ceramic or the lithium silicate glass comprise at least one of the following components in the given amounts

Component	wt.-%
SiO_2	56.9 to 72.0
Li_2O	14.2 to 18.0
Rb_2O	3.7 to 7.7
Al_2O_3	2.5 to 4.5
P_2O_5	3.1 to 5.0
ZrO_2	0 to 4.0
Transition metal oxide	0 to 7.0,

wherein the transition metal oxide is selected 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. Use according to claim 2 or 3, in which the lithium silicate glass ceramic or the lithium silicate glass comprise all of the indicated components in the given amounts.

5. Use according to any one of claims 1 to 4, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 58.0 to 72.0 wt.-% SiO_2.

6. Use according to claim 5, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 60.0 to 71.0 wt.-% SiO_2.

7. Use according to claim 6, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 63.0 to 70.0 wt.-% SiO_2.

8. Use according to any one of claims 1 to 7, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 5.1 to 7.7 wt.-% Rb_2O.

9. Use according to claim 8, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 6.1 to 7.4 wt.-% Rb_2O.

10. Use according to any one of claims 1 to 9, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 2.5 to 4.0 wt.-% Al_2O_3.

11. Use according to claim 10, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 3.0 to 3.5 wt.-% Al_2O_3.

12. Use according to claim 11, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 3.2 to 3.4 wt.-% Al_2O_3.

13. Use according to any one of claims 1 to 12, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 2.5 wt.-% Cs_2O.

14. Use according to claim 13, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 1.5 wt.-% Cs_2O.

15. Use according to claim 14, in which the lithium silicate glass ceramic or the lithium silicate glass comprise 1.0 wt.-% Cs_2O.

16. Use according to claim 15, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 0.5 wt.-% Cs_2O.

17. Use according to claim 16, in which the lithium silicate glass ceramic or the lithium silicate glass are substantially free of Cs_2O.

18. Use according to any one of claims 1 to 17, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 4.0 wt.-% Na_2O and/or K_2O.

19. Use according to claims 18, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 3.5 wt.-% Na_2O and/or K_2O.

20. Use according to claims 19, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 3.0 wt.-% Na_2O and/or K_2O.

21. Use according to claims 20, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 2.5 wt.-% Na_2O and/or K_2O.

22. Use according to claim 21, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 2.0 wt.-% Na_2O and/or K_2O.

23. Use according to any one of claims 1 to 22, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 3.8 wt.-% BaO.

24. Use according to claims 23, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 2.5 wt.-% BaO.

25. Use according to claims 24, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 1.5 wt.-% BaO.

26. Use according to claims 25, in which the lithium silicate glass ceramic or the lithium silicate glass comprise less than 0.5 wt.-% BaO.

27. Use according to claims 26, in which the lithium silicate glass ceramic or the lithium silicate glass are substantially free of BaO.

28. Use according to any one of claims 1 to 27, in which a lithium silicate glass ceramic is used which comprises lithium metasilicate as main crystal phase.

29. Use according to claim 28, in which the lithium silicate glass ceramic has a bending strength in the range of 180 to 300 MPa and/or a fracture toughness, measured as K_{IC} value, of at least 2.0 $MPa \cdot m^{0.5}$.

30. Use according to claim 29, in which the lithium silicate glass ceramic has a fracture toughness, measured as K_{IC} value, of at least 2.3 $MPa \cdot m^{0.5}$.

31. Use according to any one of claims 1 to 30, in which a lithium silicate glass ceramic is used which comprises lithium disilicate as main crystal phase.

32. Use according to claim 31, in which the lithium silicate glass ceramic has a bending strength in the range of 400

to 700 MPa and/or a fracture toughness, measured as K_{IC} value, of at least 2.0 $MPa \cdot m^{0.5}$.

33. Use according to claim 32, in which the lithium silicate glass ceramic has a fracture toughness, measured as K_{IC} value, of at least 2.3 $MPa \cdot m^{0.5}$.

34. Use according to any one of claims 1 to 33, in which a lithium silicate glass is used.

35. Use according to claims 34, wherein the lithium silicate glass comprises nuclei for forming lithium metasilicate and/or lithium disilicate crystals.

36. Use according to any one of claims 1 to 35, in which the substrate is a non-precious metal alloy.

37. Use according to any one of claims 1 to 36, in which the substrate is a dental restoration.

38. Use according to claim 37, in which the substrate is a bridge, an inlay, an onlay, a veneer, an abutment, a partial crown, a crown or a facet.

39. Process for coating a substrate selected from metals and alloys, in which the lithium silicate glass ceramic or the lithium silicate glass as defined in any one of claims 1 to 35 is applied to the substrate.

40. Process according to claim 39, in which the substrate is a non-precious metal alloy.

41. Process according to claim 39 or 40, in which the substrate is a dental restoration.

42. Process according to claim 41, in which the substrate is a bridge, an inlay, an onlay, a veneer, an abutment, a partial crown, a crown or a facet.

43. Process according to any one of claims 39 to 42, in which the lithium silicate glass ceramic or the lithium silicate glass is applied to the substrate by sintering.

44. Process according to any one of claims 39 to 42, in which the lithium silicate glass ceramic or the lithium silicate glass is applied to the substrate by pressing-on.

45. Process according to any one of claims 39 to 42, in which the lithium silicate glass ceramic or the lithium silicate glass is applied to the substrate by joining.

46. Process according to claim 45, in which the lithium silicate glass ceramic or the lithium silicate glass is shaped to a desired geometry by machining or by hot pressing before joining.

47. Process according to any one of claims 39 to 46, in which a coating is obtained which comprises a lithium silicate glass ceramic that comprises lithium metasilicate as main crystal phase.

48. Process according to any one of claims 39 to 47, in which a coating is obtained which comprises a lithium silicate glass ceramic that comprises lithium disilicate as main crystal phase.

49. Composite material which comprises the lithium silicate glass ceramic or the lithium silicate glass as defined in any one of claims 1 to 35 on a substrate selected from metals and alloys.

50. Composite material according to claim 49, in which the substrate is a non-precious metal alloy.

51. Composite material according to claim 49 or 50, in which the substrate is a dental restoration.

52. Composite material according to claim 51, in which the substrate is a bridge, an inlay, an onlay, a veneer, an abutment, a partial crown, a crown or a facet.

53. Lithium silicate glass ceramic, which comprises the following components in the given amounts

Component	wt.-%
SiO_2	56.0 to 72.5
Li_2O	13.0 to 19.0
Rb_2O	3.0 to 9.0
Al_2O_3	2.0 to 5.0
P_2O_5	2.0 to 6.0
ZrO_2	0 to 4.5
Transition metal oxide	0 to 7.5,

wherein the transition metal oxide is selected 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 and wherein the glass ceramic has a linear coefficient client of thermal expansion $CTE_{100-400°C}$ in the range of 9.0 to $14.0 \cdot 10^{-6}$ K^{-1}.

54. Lithium silicate glass ceramic according to claim 53, which comprises at least one of the following components in the given amounts

Component	wt.-%
SiO_2	56.9 to 72.0
Li_2O	14.2 to 18.0
Rb_2O	3.7 to 7.7
Al_2O_3	2.5 to 4.5
P_2O_5	3.1 to 5.0
ZrO_2	0 to 4.0
Transition metal oxide	0 to 7.0.

55. Lithium silicate glass ceramic according to claim 54, which comprises all of the indicated components in the given amounts.

56. Lithium silicate glass, which comprises the following components in the given amounts

Component	wt.-%
SiO_2	56.0 to 72.5
Li_2O	13.0 to 19.0
Rb_2O	3.0 to 9.0
Al_2O_3	2.0 to 5.0
P_2O_5	2.0 to 6.0
ZrO_2	0 to 4.5

Transition metal oxide	0 to 7.5,

wherein the transition metal oxide is selected 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 and wherein the glass has a linear coefficient of thermal expansion $CTE_{100-400°C}$ in the range of 9.0 to $14.0 \cdot 10^{-6}$ K^{-1}.

57. Lithium silicate glass according to claim 56, which comprises at least one of the following components in the given amounts

Component	wt.-%
SiO_2	56.9 to 72.0
Li_2O	14.2 to 18.0
Rb_2O	3.7 to 7.7
Al_2O_3	2.5 to 4.5
P_2O_5	3.1 to 5.0
ZrO_2	0 to 4.0
Transition metal oxide	0 to 7.0.

58. Lithium silicate glass according to claim 57, which comprises all of the indicated components in the given amounts.