



US 20230099360A1

(19) **United States**(12) **Patent Application Publication**
DURSCHANG et al.(10) **Pub. No.: US 2023/0099360 A1**(43) **Pub. Date: Mar. 30, 2023**(54) **LITHIUM DISILICATE GLASS-CERAMIC,
METHOD FOR PRODUCTION THEREOF
AND USE THEREOF**(30) **Foreign Application Priority Data**

Dec. 23, 2009 (DE) 10 2009 060 274.7

(71) Applicants: **FRAUNHOFER-GESELLSCHAFT
zur Förderung der angewandten
Forschung e.V.**, München (DE); **VITA
Zahnfabrik H. Rauter GmbH & Co.
KG**, Bad Säckingen (DE); **DeguDent
GmbH**, Hanau (DE)**Publication Classification**(51) **Int. Cl.**

<i>A61K 6/818</i>	(2020.01)
<i>A61K 6/833</i>	(2020.01)
<i>A61C 5/70</i>	(2017.01)
<i>A61C 13/083</i>	(2006.01)
<i>C03C 4/00</i>	(2006.01)
<i>A61C 13/00</i>	(2006.01)
<i>A61C 13/01</i>	(2006.01)
<i>C03B 32/02</i>	(2006.01)
<i>A61C 5/35</i>	(2017.01)
<i>C03C 10/00</i>	(2006.01)
<i>A61K 6/82</i>	(2020.01)
<i>C03C 3/097</i>	(2006.01)
<i>A61C 5/77</i>	(2017.01)

(72) Inventors: **Bernhard DURSCHANG**, Rottendorf (DE); **Jörn PROBST**, Kürnach (DE); **Norbert THIEL**, Bad Säckingen (DE); **Joachim BIBUS**, Bad Säckingen (DE); **Markus VOLLMANN**, Gelnhausen (DE); **Udo SCHUSSER**, Alzenau (DE)(52) **U.S. Cl.**

CPC *A61K 6/818* (2020.01); *A61K 6/833* (2020.01); *A61C 5/70* (2017.02); *A61C 13/083* (2013.01); *C03C 4/0021* (2013.01); *A61C 13/0006* (2013.01); *A61C 13/01* (2013.01); *C03B 32/02* (2013.01); *A61C 5/35* (2017.02); *C03C 10/0027* (2013.01); *A61K 6/82* (2020.01); *C03C 3/097* (2013.01); *A61C 5/77* (2017.02)

(73) Assignees: **FRAUNHOFER-GESELLSCHAFT
zur Förderung der angewandten
Forschung e.V.**, München (DE); **VITA
Zahnfabrik H. Rauter GmbH & Co.
KG**, Bad Säckingen (DE); **DeguDent
GmbH**, Hanau (DE)(21) Appl. No.: **17/852,126**(22) Filed: **Jun. 28, 2022****Related U.S. Application Data**

(63) Continuation of application No. 17/012,113, filed on Sep. 4, 2020, now abandoned, which is a continuation of application No. 16/227,429, filed on Dec. 20, 2018, now Pat. No. 10,765,496, which is a continuation of application No. 14/274,235, filed on May 9, 2014, now Pat. No. 10,219,879, which is a continuation of application No. 13/518,765, filed on Aug. 15, 2012, now Pat. No. 8,956,987, filed as application No. PCT/EP10/07918 on Dec. 23, 2010.

(57)

ABSTRACT

The invention relates to glass-ceramics based on the lithium silicate system which can be mechanically machined easily in an intermediate step of crystallization and, after complete crystallisation, represent a very strong, highly-translucent and chemically-stable glass-ceramic. Likewise, the invention relates to a method for the production of these glass-ceramics. The glass-ceramics according to the invention are used as dental material.

**LITHIUM DISILICATE GLASS-CERAMIC,
METHOD FOR PRODUCTION THEREOF
AND USE THEREOF**

[0001] This application claims priority to and is a continuation of U.S. application Ser. No. 17/012,113 filed Sep. 4, 2020, which published as US Publication No. 2021/0055157, which is a continuation of U.S. application Ser. No. 16/227,429 filed Dec. 20, 2018, which published as US Publication No. 2019/0142556, now U.S. Pat. No. 10,765,496, which is a continuation of U.S. application Ser. No. 14/274,235 filed May 9, 2014, which published as US Publication No. 2014/0249016 on Sep. 4, 2014, now U.S. Pat. No. 10,219,879, which is a continuation of U.S. application Ser. No. 13/518,765 filed Aug. 15, 2012, which published as U.S. Publication No. 2012/0309607, now U.S. Pat. No. 8,956,987, which is the national state entry of PCT/EP10/07918 filed Dec. 23, 2010, which claims priority to DE 10 2009 060 274.4 filed Dec. 23, 2009, all of which are hereby incorporated by reference in their entirety.

[0002] The invention relates to glass-ceramics based on the lithium disilicate system which can be mechanically machined easily in an intermediate step of crystallisation and, after complete crystallisation, represent a very strong, highly-translucent and chemically-stable glass-ceramic. Likewise, the invention relates to a method for the production of these glass-ceramics. The glass-ceramics according to the invention are used as dental material.

[0003] Lithium disilicate glass-ceramics are well known from the literature and several patents are based on this glass-ceramic system. Thus, for example, self-glazed lithium disilicate glass-ceramic objects for the production of tableware are described in EP-B-536 479, in EP-B-536 572 lithium disilicate glass-ceramics which can be used, by scattering fine-particle coloured glass on the surface thereof, as lining elements for building purposes.

[0004] The main focus of patented lithium disilicate glass-ceramics is on dental applications. This is due to the fact that the crystallisation of lithium disilicate crystals is effected via a phase of lesser strength (lithium metasilicate) and the material system is consequently amenable inter alia to chair-side methods (see S.D. Stookey: "Chemical Machining of Photosensitive Glass", Ind. Eng. Chem., 45, pp. 115-118 (1993) and S. D. Stookey: "Photosensitively Opacifiable Glass" U.S. Pat. No. 2,684,911 (1954)). Investigations by Borom, e.g. M.-P. Borom, A. M. Turkalo, R. H. Doremus: "Strength and Microstructure in Lithium Disilicate Glass-Ceramics", J. Am. Ceram. Soc., 58, No. 9- 10, pp. 385-391 (1975) and M.-P. Borom, A. M. Turkalo, R. H. Doremus: "Verfahren zum Herstellen von Glaskeramiken" (Method for the production of glass-ceramics), DE-A-24 51 121 (1974) show that glass-ceramics which comprise lithium metasilicate as main phase have reduced strength in comparison with glass-ceramics which comprise lithium disilicate as single crystalline phase.

[0005] This principle was used in order firstly to produce a glass-ceramic, in a two-step crystallisation process, which can be machined well mechanically, e.g. by means of CAD/CAM methods, and to process this subsequently in a second crystallisation step to form dental glass-ceramic. This method is suitable for being able to use dental restorations according to the so-called chair-side method. In the case of this method, an individually adapted crown/onlay/inlay is milled out of a glass-ceramic block after the first crystallisation step by means of CAD/CAM in the dentist's

surgery, this is subjected to the second crystallisation step in a special oven and used directly in the first and only dental appointment for the patient (DE 10 2005 028 637).

[0006] In addition, in WO-A-95/32678 and U.S. Pat. No. 5,507,981, lithium disilicate glass-ceramics were described, which can be processed to form shaped dental products by means of hot-pressing by using a special compressible crucible. Furthermore, there are known, from DE-C-14 21 886, glass-ceramics based on SiO_2 and Li_2O which contain large quantities of physiologically very questionable arsenic oxide. Also in U.S. Pat. No. 4,515,634 and in FR-A-2 655 264, lithium disilicate glass-ceramics which are suitable for the production of dental crowns and bridges are disclosed.

[0007] All known lithium disilicate glass-ceramics display inadequacies in the processing thereof to shaped products and/or in mechanical or visual properties and/or in chemical stability. In particular when used in the dental field, equally high requirements for all the mentioned properties must be fulfilled.

[0008] Starting herefrom, it was the object of the present invention to provide a glass-ceramic which has improved mechanical and optical properties and also improved chemical stability relative to the (glass-) ceramics known from the state of the art.

[0009] This object is achieved by the lithium disilicate glass-ceramic having the features of at least 10% by weight of a stabilizer in order to increase the chemical and mechanical stability, the stabilizer begin present essentially in the amorphous phase and also by the method for the production of this glass-ceramic having the features in which a) an initial glass is produced which comprises the components of the glass-ceramic, b) the initial glass is subjected to a first heat treatment in order to produce a glass-ceramic which has lithium metasilicate as main crystal phase, c) the glass-ceramic of b) is subjected to a second heat treatment in which the lithium metasilicate is converted with SiO_2 from the glass phase into lithium disilicate and subsequently lithium disilicate is present as main crystal phase. Uses according to the invention as dental material or as a component of a dental material are indicated. Likewise, a shaped dental product having the features of an inlay, an onlay, a bridge, a pin construction, a veneer, and a (partial) crown is provided.

[0010] Within the scope of the present invention, glass compositions have been developed which can be prepared in a two-step production process, are easy to machine after the first crystallisation step, in particular by means of CAD/CAM, and, after a very short second crystallisation step, are both highly-transparent and very strong and have better chemical stabilities than the known lithium disilicate glass-ceramics.

[0011] It was shown surprisingly that the addition of at least 10 wt % ZrO_2 to certain glass compositions leads to glass-ceramics which can be machined very readily in an intermediate crystallisation step and, in the end state, have excellent strength values, exceptional translucence and significantly increased chemical stabilities.

[0012] It was shown that up to 20% by weight of a stabiliser selected from the group consisting of ZrO_2 , HfO_2 or mixtures hereof can be incorporated in the glass without having a significant influence on the structure. Contrary to all expectations, the stabiliser does not hereby crystallise out as a separate crystal phase but remains in the remaining glass phase. As a result of the high proportion in the amorphous

phase, the mechanical and chemical stabilities in this phase are hugely improved, which also leads to improved properties in the end product.

[0013] In particular the chemical stability can be improved via the composition of the remaining glass phase since the glass phase has a significantly higher solubility than the lithium disilicate and hence represents the weak point with respect to chemical attack. The extremely high solubility of the stabiliser (ZrO_2) in the glass phase is in particular remarkable since e.g. zirconium oxide acts in many silicate glass-ceramics as nucleation agent, i.e. crystallises out as first phase during a temperature treatment, and the actually sought crystal phase is facilitated and is deposited in a fine-crystalline manner on these ZrO_2 crystals.

[0014] As a result of the high proportions of stabiliser which remain essentially in the amorphous phase, the crystalline proportion is correspondingly restricted. As a result, and due to the low crystallite size of the lithium disilicate crystals, good translucence of the materials is produced after the second crystallisation. The translucence is however also further improved by the refractive index of the glass phase being increased in turn by the stabiliser and, consequently, being adapted to the refractive index of the lithium disilicate. In the case of glass-ceramics in which the refractive index of the amorphous matrix phase corresponds to the refractive index of the crystalline phase/phases, very good translucence properties are found, relatively irrespective of the crystallite size. In the glass-ceramics according to the invention, therefore all three points for the production of an extremely translucent glass-ceramic are fulfilled:

[0015] limited crystal phase proportion,

[0016] small crystals (<500 nm),

[0017] adapted refractive index of amorphous and crystalline phase.

[0018] The high proportion of stabiliser has the effect therefore in the glass-ceramic of

[0019] improved chemical stability,

[0020] higher strength values and

[0021] improved translucence in several respects

to corresponding glass-ceramics without or with only a low ZrO_2 - or HfO_2 proportion.

[0022] The glass-ceramics according to the invention can be produced preferably by means of a method, in which

[0023] a) an initial glass is produced which comprises the components of the glass-ceramic,

[0024] b) the initial glass is subjected to a first heat treatment at a first temperature in order to produce a glass-ceramic which has lithium metasilicate as single or main crystal phase and

[0025] c) this glass-ceramic is subjected to a second heat treatment in which the lithium metasilicate is converted with SiO_2 from the glass phase into lithium disilicate and subsequently lithium disilicate is present as single or main crystal phase.

[0026] The crystallisation to form lithium metasilicate preferably takes place at temperatures between 620° C. and

800° C., with times between 1 and 200 minutes, preferably between 650° C. and 750° C. for 10 to 60 minutes.

[0027] The crystallisation to form lithium disilicate preferably takes place at temperatures between 800° C. and 1,040° C., with times of 5 to 200 minutes, preferably between 800° C. and 870° C. for 5 to 30 minutes.

[0028] The subject according to the invention is intended to be explained in more detail with reference to the subsequent examples without wishing to restrict said subject to the special embodiments shown here.

EXAMPLES 1 to 6

[0029] In examples 1 to 6, compositions of glasses with a high zirconium oxide content are indicated, which are converted by a two-step temperature treatment firstly into readily mechanically machinable lithium metasilicate glass-ceramics and subsequently into highly-translucent, very strong and chemically-stable lithium disilicate glass-ceramics.

[0030] The compositions with their components are represented in Table 1.

TABLE 1

	81	82	83	84	85	86
SiO_2	66.9	65.8	65.5	63.7	63.5	63.5
Li_2O	13.9	13.7	13.6	13.2	14.4	12.9
ZrO_2	10.0	10.0	12.0	11.7	12.7	13.5
Al_2O_3	3.2	3.1	3.1	3.0	3.3	3.5
P_2O_5	3.0	3.0	3.0	2.9	3.1	3.4
K_2O	2.9	2.9	2.9	2.8	3.0	3.2
CeO_2	—	1.0	—	2.0	—	—
Er_2O_3	—	0.2	—	0.3	—	—
Tb_2O_3	—	0.3	—	0.3	—	—

[0031] The glasses were melted at 1,500° C. and poured into metal moulds to form blocks. The blocks were stress-relieved at 560° C. in the furnace and cooled slowly. For the different characterisation processes, the glass blocks were divided up and subjected to a first crystallisation treatment. For this purpose, the glasses were aged for 10 to 120 minutes at 600° C. to 750° C. As a result, glass-ceramics with strength values of 150 MPa to 220 MPa were produced. Exclusively lithium metasilicate was hereby established as crystal phase. In this state, machining by means of CAD/CAM methods is very readily possible.

[0032] With a second short crystallisation at 800° C. to 950° C. for 3 to 15 minutes, recrystallisation of the lithium metasilicate with amorphous SiO_2 from the glass phase takes place to form lithium disilicate and the result is an increase in strength to 300 MPa to 450 MPa. In addition to the lithium disilicate phase, a subsidiary crystal phase with a zirconium oxide content can hereby be produced. In addition, also small residues of lithium metasilicate can be present. The unequivocal main crystal phase is lithium disilicate.

[0033] In Table 2, the crystallisation conditions of individual glasses and also the resulting crystal phases and strength values are displayed.

TABLE 2

Glass	81	82	83	84	85	86
1. Crystallisation	650° C. 20 min	700° C. 40 min	650° C. 30 min	700° C. 20 min	700° C. 40 min	700° C. 40 min

TABLE 2-continued

Glass	81	82	83	84	85	86
2. Crystallisation	850° C. 10 min	830° C. 10 min	870° C. 20 min	850° C. 8 min	820° C. 10 min	830° C. 10 min
<u>Crystal phases</u>						
Main phase (>80%)	disilicate	disilicate	disilicate	disilicate	disilicate	disilicate
Subsidiary phase (<20%)	—	—	—	—	metasilicate	metasilicate
Translucence	excellent	very good	excellent	very good	excellent	excellent
3-point bending strength	375 MPa	413 MPa	380 MPa	418 MPa	356 MPa	385 MPa

1. (canceled)

2. A method of producing a shaped lithium disilicate dental product, comprising:

a) producing an initial glass, wherein the amount of SiO₂ is 55 to 70 weight percent, the amount of Li₂O is 10 to 15 weight percent, the amount of K₂O is 0.1 to 5 weight percent, the amount of Al₂O₃ is 0.1 to 5 weight percent, the amount of P₂O₅ is 2 to 5 weight percent, and the amount of ZrO₂ is at least 10.0 weight percent, wherein the total weight percent is 100 weight percent;

b) subjecting the initial glass to a first heat treatment in order to produce a glass-ceramic which has lithium metasilicate as the main crystal phase;

c) forming a shaped dental product out of the glass-ceramic; and

d) forming a shaped lithium disilicate dental product by subjecting the shaped dental product to a second heat treatment in which the lithium metasilicate is converted with SiO₂ from the glass phase into lithium disilicate and subsequently lithium disilicate is present as the main crystal phase.

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