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(54) Title: LITHIUM SILICATE GLASSES OR GLASS CERAMICS, METHOD FOR PRODUCTION THEREOF AND USE THEREOF

(57) Abrégé/Abstract:
The invention relates to glass ceramics based on the lithium metasilicate system ($Li_2O$ $SiO_2$ ($Li_2SiO_3$) ), which are mechanically processible in a simple manner in an intermediate stage of the crystallization and, after complete crystallization, represent a high-strength, highly translucent and chemically stable glass ceramic.

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(54) Title: LITHIUM SILICATE GLASSES OR GLASS CERAMICS, METHOD FOR PRODUCTION THEREOF AND USE THEREOF

(57) Abstract: The invention relates to glass ceramics based on the lithium metasilicate system ($Li_2O$ $SiO_2$ ($Li_2SiO_3$) ), which are mechanically processible in a simple manner in an intermediate stage of the crystallization and, after complete crystallization, represent a high- strength, highly translucent and chemically stable glass ceramic.

# Lithium silicate glasses or glass ceramics, method for production thereof and use thereof

The invention relates to glass ceramics based on the lithium metasilicate system ($Li_2O \cdot SiO_2$ ($Li_2SiO_3$)), which are mechanically processible in a simple manner in an intermediate stage of the crystallization and, after complete crystallization , represent a high-strength, highly translucent and chemically stable glass ceramic.

In the lithium oxide-silicon dioxide system, lithium disilicate ($Li_2O \cdot 2\ SiO_2$ ($Li_2Si_2O_5$))-glass ceramics are well known from the literature and several patents are based on this glass ceramic system. For example, in EP-B-536 479, self-glazed lithium disilicate glass ceramic objects are thus described for the

production of tableware and, in EP-B-536 572, lithium disilicate glass ceramics which can be used by scattering a fine-particle coloured glass onto the surface thereof as cladding elements for building purposes,

A main focus of the patented lithium disilicate glass ceramics resides in dental applications. The lithium disilicate system is very suitable here for the production of CAD/CAM-processible glass ceramics since the crystallization is effected here via the lithium metasilicate phase (see S. D. Stookey: "Chemical Machining of Photosensitive Glass", Ind. Eng. Chem., 45, 115 - 118 (1993) and S. D. Stookey: "Photosensitively Opacifiable Glass" US-A-2 684 911 (1954)). These lithium metasilicate glass ceramics have such low strengths in this intermediate stage that they can be readily processed by means of CAD/CAM (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, 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)). Only by the subsequent conversion to form lithium disilicate in a second crystallization stage are dental materials with high strengths achieved.

This principle is exploited in order to produce firstly a glass ceramic, in a two-stage crystallization process, which glass ceramic can be readily processed mechanically, e.g. by means of CAD/CAM

processes, and in order to process this subsequently in a second crystallization stage to form dental glass ceramic. This method is suitable in order to be able to use dental restorations according to the so-called chair-side method. In this method, an individually adapted crown/onlay/inlay is milled out of a glass ceramic block after the first crystallization stage by means of CAD/CAM, in the dental practice this is subjected to the second crystallization stage in a special oven and used directly in the first and only dentist's visit for the patient (DE 10 2005 028 637). An application by the dental technician in the pressing method or in mechanical processing with subsequent characterisation or individualisation whilst taking into account suitable paints or layer ceramics can also be effected.

Starting herefrom, it was the object of the present invention to provide glass ceramics which have improved strength values and also improved translucence and chemical resistance.

This object is achieved by the lithium silicate glasses or glass ceramics having the features of claim 1, the method for producing a dental restoration having the features of claim 17 and a shaped dental restoration of claim 20. The use of the lithium silicate glasses or glass ceramics is described in claim 19. The further dependent claims reveal advantageous developments.

Within the scope of the present invention, glass compositions were developed in the basic system $SiO_2$-$Li_2O$-$ZrO_2$, which have lithium metasilicate as only or as main crystal phase (> 50%). %). Hereby, zirconia acts as a stabilizer of the residual glassy phase and can be completely or partially replaced by oxides of Hafnium, Germanium, Cerium, Lanthanum, Yttrium, Titanium and zinc.

Surprisingly, it was shown that lithium metasilicate glass ceramics which have excellent strength values, exceptional translucence and very good chemical resistances can be produced in this system.

It was shown in addition that up to 20% by weight of $ZrO_2$ or other stabilizers can be incorporated in the glass without the structure being significantly influenced. Contrary to all expectations, the $ZrO_2$ or other stabilizers does not hereby crystallise as a separate crystal phase but remains completely or extensively in the amorphous residual glass phase. Because of the high proportion of $ZrO_2$ or other stabilizers, the mechanical and chemical resistances are hugely improved in this amorphous phase, which also leads to improved properties in the entire dental glass ceramic (crystal phase(s) and residual glass phase), such as for example final strength and acid solubility.

The method is also suitable for a two-stage production process from the initial glass, a partial crystallization of the lithium metasilicate being ef-

fected in the first processing stage, which enables good CAD/CAM processing. In the second processing stage, an increase in the crystal phase proportion (primary lithium metasilicate) is effected, which leads to the high strength values. The most important cause of the surprisingly high strengths in the lithium metasilicate system is hereby ascribed to the high zirconium oxide or other stabilizers proportion (> 8 MA).

High translucence is ensured via the low crystallite size in the glass ceramics. In addition, good chemical stability is ensured by the high zirconium oxide proportion in the glass phase and the enriched amount of $SiO_2$ in the residual glassy phase compared to lithiumdisilicate-glass-ceramics (Lithiumdisilicate = Lithiummetasilicate + $SiO_2$).

According to the invention, lithium silicate glasses or glass ceramics with the following composition are provided:

50 to 75 wt-% $SiO_2$,
10 to 25 wt-% $Li_2O$,
5 to 30 wt-% of a stabilizer selected from the group consisting of the oxides of Zr, Hf, Ge, La, Y, Ce, Ti, Zn or its mixtures,
0 to 8 wt-% $K_2O$ and/or $Na_2O$,
0 to 8 wt-% $Al_2O_3$, and
0 to 15 wt-% additives.

Preferably, the glasses or glass ceramics have the following composition:

50 to 75 wt-% $SiO_2$,
10 to 25 wt-% $Li_2O$,
5 to 30 wt-% of a stabilizer selected from the group consisting of $ZrO_2$ and/or $HfO_2$,
0 to 8 wt-% $K_2O$ and/or $Na_2O$,
0 to 8 wt-% $Al_2O_3$, and
0 to 15 wt-% additives.

More preferably, the glasses or glass ceramics have the following composition:

50 to 70 wt-% $SiO_2$,
15 to 22 wt-% $Li_2O$,
8 to 20 wt-% of a stabilizer selected from the group consisting of the oxides of Zr, Hf, Ge, La, Y, Ce, Ti, Zn or its mixtures,
0,1 to 4 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 4 wt-% $Al_2O_3$, and
2 to 8 wt-% additives.

In a preferred embodiment, the glasses or glass ceramics have the following composition:

50 to 70 wt-% $SiO_2$,
15 to 22 wt-% $Li_2O$,
8 to 20 wt-% of a stabilizer selected from the group consisting of $ZrO_2$ and/or $HfO_2$,
0,1 to 4 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 4 wt-% $Al_2O_3$, and
2 to 8 wt-% additives.

In a further preferred embodiment, the glasses or

glass ceramics have the following composition:

50 to 64 wt-% $SiO_2$,
17 to 20 wt-% $Li_2O$,
8 to 20 wt-% of a stabilizer selected from the group consisting of $ZrO_2$ and/or $HfO_2$,
1 to 3 wt-% $K_2O$ and/or $Na_2O$,
1 to 3 wt-% $Al_2O_3$, and
4 to 6 wt-% additives.

In a further preferred embodiment the glasses or glass ceramics have the following composition:

55 to 64% by weight of $SiO_2$,
10 to 20% by weight of $Li_2O$,
8 to 20% by weight of a stabilizer selected from the group consisting of $ZrO_2$, $HfO_2$ or mixtures hereof,
0 to 5% by weight of $K_2O$ and/or $Na_2O$,
0,1 to 5% by weight of $Al_2O_3$ and also 0 to 10% by weight of additives.

In a further preferred embodiment the glasses or glass ceramics have the following composition:

55 to 60% by weight of $SiO_2$,
10 to 20% by weight of $Li_2O$,
8 to 20% by weight of a stabilizer selected from the group consisting of $ZrO_2$, $HfO_2$ or mixtures hereof,
0 to 5% by weight of $K_2O$ and/or $Na_2O$,
0,1 to 5% by weight of $Al_2O_3$ and also 0 to 10% by weight of additives.

Furthermore, a glass or a glass ceramic with the following composition is preferred:

55 to 64% by weight of $SiO_2$,
10 to 20% by weight of $Li_2O$,
10 to 20% by weight of a stabilizer selected from the group consisting of $ZrO_2$, $HfO_2$ or mixtures hereof,
0 to 5% by weight of $K_2O$ and/or $Na_2O$,
0,1 to 5% by weight of $Al_2O_3$ and also
0 to 10% by weight of additives.

A further preferred composition comprises

55 to 60% by weight of $SiO_2$,
10 to 20% by weight of $Li_2O$,
10 to 20% by weight of a stabilizer selected from the group consisting of $ZrO_2$, $HfO_2$ or mixtures hereof,
0 to 5% by weight of $K_2O$ and/or $Na_2O$,
0,1 to 5% by weight of $Al_2O_3$ and also
0 to 10% by weight of additives.

The stabilizer is preferably $ZrO_2$ and/or $HfO_2$. Preferably, the stabilizer is essentially present in an amorphous state.

There may be contained as additives, components selected from the group consisting of nucleation agents, fluorescent agents, dyes, in particular glass-colouring oxides, coloured pigments and mixtures thereof, in the glass or in the glass ceramic.

As for all glasses and glass-ceramics, some compo-

nents have effects on several properties. For example, titania can act as nucleation and colouring agent. Most of the rare earth metal oxides show effects on colour and fluorescence. Some components can be simultaneously amorphous, incorporated in crystalline phases and build own crystalline phases.

The nucleating agents are preferably selected from the group consisting of phosphorous oxide, titanium oxide, tin oxide, mixtures thereof, and noble metals, preferably in an amount of 1 to 10 wt-%, more preferably 2 to 8 wt-% and most preferably 4 to 8 wt-%.

The fluorescent agents are preferably selected from the group consisting of oxides of bismuth, rare earth elements as neodymium, praseodymium, samarium, erbium, and europium, and mixtures thereof, preferably in an amount of 0,1 to 5 wt-%, more preferably 0,5 to 4 wt-% and most preferably 1 to 3 wt-%.

The glass colouring oxides are preferably selected from the group of oxides of iron, titanium, cerium, copper, chromium, cobalt, nickel, manganese, selenium, silver, indium, gold, vanadium, rare earth elements as neodymium, praseodymium, samarium, europium, terbium, dysprosium, holmium, erbium, yttrium, and mixtures thereof, preferably in an amount of 0,1 to 6 wt-%, more preferably 0,5 to 5 wt-% and most preferably 1 to 4 wt-%.

The coloured pigments can be doped spinels, which are comprised preferably in an amount of 0,1 to 6 wt-%, more preferably 0,5 to 5 wt-% and most preferably 1 to 4 wt-%.

Further additives are preferably selected from the group consisting of boron oxide, phosphorus oxide, fluorine, sodium oxide, barium oxide, strontium oxide, magnesium oxide, zinc oxide, calcium oxide, yttrium oxide, titanium oxide, niobium oxide, tantalum oxide, lanthanum oxide and mixtures thereof, which are comprised preferably in an amount of 0,1 to 5 wt-%.

According to the invention, a method for the above-described lithium silicate glasses or glass ceramics and a method for producing a dental restoration comprising the above-described lithium silicate glass or glass ceramic is likewise provided, wherein

a) an glass is provided as starting material which comprises the components of the glass ceramic,

b) the glass is subjected to a first heat treament for producing a glass ceramic which comprises lithium metasilicate as exclusive or main crystal phase,

c) the glass ceramic of b) is subjected to a second heat treatment, wherein further metasilicate is segregated from the glass phase. The lithium metasilicate is present as main crystal phase.

The first heat treatment is thereby effected preferably at a temperature of 620°C to 950°C over a period of time of 1 to 200 minutes. It is particularly preferred to implement the first heat treatment at temperatures of 650°C to 750°C over a period of time of

10 to 60 minutes.

The further crystallization of the lithium metasilicate takes place preferably at temperatures between 800°C and 1,040°C over a period of time of 5 to 200 minutes, particularly preferred between 800°C and 870°C over a period of time of 5 to 30 minutes.

The lithium silicate glasses or glass ceramics according to the invention are used as dental material or as component of a dental material.

According to the invention, a shaped dental product which comprises the previously-described lithium silicate glass or the lithium silicate glass ceramic is likewise provided. The shaped dental products are thereby present in particular in the form of an inlay, an onlay, a bridge, an abutment, a facing, a veneer, a facet, a crown, a partial crown, a framework or a coping.

The lithium silicate glasses or glass ceramics with the following compositions are further aspects of the present invention:

Composition 1

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 2

| | |
|---|---|
| $SiO_2$ | 50 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 3

| | |
|---|---|
| $SiO_2$ | 55 to 60 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 4

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 15 to 22 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 5

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 17 to 20 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 6

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 8 to 20 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 7

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 10 to 15 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 8

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0,1 to 5 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 9

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 1 to 3 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 15 wt-% |

Composition 10

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0,1 to 5 wt-% |
| additives | 0 to 15 wt-% |

Composition 11

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 1 to 3 wt-% |
| additives | 0 to 15 wt-% |

Composition 12

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 1 to 10 wt-% |

Composition 13

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 2 to 8 wt-% |

Composition 14

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 4 to 6 wt-% |

Composition 15

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 16

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 2 to 8 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 7 wt-% |

Composition 17

| | |
|---|---|
| $SiO_2$ | 50 to 75 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 4 to 6 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 9 wt-% |

Composition 18

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 19

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 15 to 22 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 20

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 17 to 20 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 21

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 8 to 20 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 22

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 8 to 15 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 23

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 5 to 30 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0,1 to 5 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 24

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 8 to 20 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 1 to 3 wt-% |
| $K_2O$ | 0 to 8 wt-% |
| additives | 0 to 5 wt-% |

Composition 25

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 8 to 20 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 0,1 to 5 wt-% |
| additives | 0 to 5 wt-% |

Composition 26

| | |
|---|---|
| $SiO_2$ | 55 to 64 wt-% |
| $Li_2O$ | 10 to 25 wt-% |
| $ZrO_2$ | 8 to 20 wt-% |
| $P_2O_5$ | 1 to 10 wt-% |
| $Al_2O_3$ | 0 to 8 wt-% |
| $K_2O$ | 1 to 3 wt-% |
| additives | 0 to 5 wt-% |

The subject according to the application is intended to be explained in more detail with reference to the subsequent figures and examples without restricting said subject to these variants.

Fig. 1 is a Scanning Electron microscope (SEM) micrograph of a glass ceramic known from the prior art.

Fig. 2 is a Scanning Electron microscope (SEM) micrograph of a glass ceramic according to the present invention.

Fig. 3 is a Scanning Electron microscope (SEM) micrograph of a glass ceramic with a low content of stabilizer.

As can be seen from the figures, the glass ceramic according to the present invention shows much better results resulting in a higher translucency as the prior art glass ceramic of Fig. 1.

The glass ceramic of Fig. 3 has a lower amount of stabilizer (4 wt-%) and shows a number of white spots of the stabilizer ($ZrO_2$) which results opaque ceramic which is undesirable in the dental field.

**Example 1**

In Table 1, compositions which are given by way of example are mentioned, from which high zirconium oxide-containing metasilicate glass ceramics can be produced for the dental field.

**Table 1** (Data in % by weight)

| | G1 | G2 | G3 | G4 | G5 | G6 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 63.5 | 63.5 | 59.0 | 59.0 | 63.5 | 63.5 |
| $Li_2O$ | 12.9 | 13.9 | 18.0 | 19.0 | 12.9 | 12.9 |
| $ZrO_2$ | 10.0 | 9.0 | 12.0 | 12.0 | 12.3 | 11.0 |
| $Al_2O_3$ | 4.7 | 5.1 | 4.5 | 4.5 | 3.9 | 4.4 |
| $P_2O_5$ | 4.5 | 4.5 | 3.5 | 3.5 | 3.7 | 4.2 |
| $K_2O$ | 4.4 | 4.0 | 3.0 | 2.0 | 3.6 | 4.0 |

The glasses were melted at 1,500°C and poured into metal moulds to form blocks. The blocks were stress-relieved in the oven at 560°C and cooled down slowly. For the various characterisation processes, the glass blocks were divided up and subjected to a first crystallization treatment. For this purpose, the glasses were stored for 10 to 120 minutes at 600°C to 750°C. As a result of this, glass ceramics with strength values of 150 MPa to 220 MPa (measured according to DIN ISO 6872) were produced. Exclusively lithium metasilicate was hereby established as crystal phase. In this state, processing by means of CAD/CAM methods is possible very readily.

With a second short crystallization at 800°C to 950°C for 3 to 15 minutes, the crystallization is continued and the result is an increase in strength from 300 MPa to 450 MPa (measured according to DIN ISO 6872). In addition to the lithium metasilicate phase, a zirconium oxide-containing subsidiary crystal phase can hereby be produced. Also a small conversion of lithium metasilicate into lithium disilicate is possible. The unambiguous main crystal phase remains the lithium metasilicate.

In Table 2, the crystallization conditions of individual glasses and also the resulting crystal phases and strength values are displayed.

**Table 2**

| Glass | G1 | G2 | G3 | G4 | G5 | G6 |
|---|---|---|---|---|---|---|
| 1. Crystallization | 680°C<br>10 min | 700°C<br>40 min | 690°<br>120 min | 620°C<br>120 min | 680°C<br>20 min | 700°C<br>20 min |
| 2. Crystallization | 820°C<br>15 min | 850°C<br>10 min | 870°C<br>10 min | 880°C<br>8 min | 830°C<br>15 min | 830°C<br>10 min |
| Crystal phases<br>- main phase (> 80%)<br>- subsidiary phase (< 20%) | metasili-cate<br>- | metasili-cate<br>- | metasili-cate<br>$ZrO_2$-containing | metasili-cate<br>$ZrO_2$-containing | metasili-cate<br>disilicate | metasili-cate<br>disilicate |
| Translucence | excellent | excellent | very good | very good | excellent | excellent |
| 3-point bending strength | 322 MPa | 418 MPa | 430 MPa | 323 MPa | 403 MPa | 402 MPa |

**Example 2**

In Table 3, fixed compositions given by way of example for different stabilizer is mentioned, from which high stabilizer-containing metasilicate glass ceramics can be produced for the dental field.

**Table 3**

| | in % by weight |
|---|---|
| $SiO_2$ | 60.0 |
| $Li_2O$ | 19.0 |
| $P_2O_5$ | 6,0 |
| $Al_2O_3$ | 2,0 |
| $K_2O$ | 2,0 |
| $CeO_2$ | 1,0 |
| Stabilizer SX* | 10,0 |

* SX represent compositions of the stabilizer S1 to S5 (s. table 4)

Table 4 shows stabilizers used by way of example for dental applications with the composition of table 1.

**Table 4**

| Stabilizers SX | |
|---|---|
| S1 | Zirconium oxide: 10 % |
| S2 | Germanium oxide: 10 % |
| S3 | Lanthanum oxide: 10 % |
| S4 | Yttrium oxide: 10 % |
| S5 | Zirconium oxide: 6 %<br>Titanium oxide: 4 % |

The glasses were melted at 1,500°C and poured into metal moulds to form blocks. The blocks were stress-relieved in the oven at 560°C and cooled down slowly. For the various characterisation processes, the glass blocks were divided

up and subjected to a first crystallization treatment. For this purpose, the glasses were stored for 10 to 120 minutes at 600°C to 750°C. As a result of this, 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, processing by means of CAD/CAM methods is possible very readily.

With a second short crystallization at 800°C to 950°C for 3 to 15 minutes, the crystallization is continued and the result is an increase in strength from 300 MPa to 450 MPa. In addition to the lithium metasilicate phase, a zirconium oxide-containing subsidiary crystal phase can hereby be produced. Also a small conversion of lithium metasilicate into lithium disilicate is possible. The unambiguous main crystal phase remains the lithium metasilicate.

In Table 5, the crystallization conditions of individual glasses and also the resulting crystal phases and strength values are shown for different stabilizers.

**Table 5**

| | S1 | S2 | S3 | S4 | S5 |
|---|---|---|---|---|---|
| Crystallization 1 | 620°C/60min | 540°C/60min | 615°C/60min | 620°C/60min | 620°C/60min |
| Crystallization 2 | 850°C/8 min | 820°C/8 min | 800°C/8 min | 820°C/8 min | 820°C/8 min |
| Crystal phases | **Li-metasilicate,** (Li-disilicate, Li-phosphate) | | | | |
| Translucency | exellent | very good | very good | exellent | Good |
| 3-point-bending strength | 418 MPa | 341 MPa | 325 MPa | 363 MPa | 358 MPa |

## Amended Claims

1. Lithium silicate glasses or glass ceramics with the following composition:
50 to 70 wt-% $SiO_2$,
15 to 22 wt-% $Li_2O$,
8 to 20 wt-% of a stabilizer selected from $ZrO_2$ and/or $HfO_2$,
0,1 to 4 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 4 wt-% $Al_2O_3$, and
2 to 8 wt-% additives.

2. Glasses or glass ceramics of claim 1 with the following composition:
50 to 64 wt-% $SiO_2$,
17 to 20 wt-% $Li_2O$,
8 to 20 wt-% of a stabilizer selected from $ZrO_2$ and/or $HfO_2$,
1 to 3 wt-% $K_2O$ and/or $Na_2O$,
1 to 3 wt-% $Al_2O_3$, and
4 to 6 wt-% additives.

3. Glasses or glass ceramics of any of the preceding claims with the following composition:
55 to 64 wt-% $SiO_2$,
10 to 20 wt-% $Li_2O$,
8 to 20 wt-% of a stabilizer selected from $ZrO_2$ and/or $HfO_2$,
0 to 5 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 5 wt-% $Al_2O_3$, and
0 to 10 wt-% additives.

4. Glasses or glass ceramics of any of the preceding claims with the following composition:
55 to 60 wt-% $SiO_2$,
10 to 20 wt-% $Li_2O$,

8 to 20 wt-% of a stabilizer selected from $ZrO_2$ and/or $HfO_2$,
0 to 5 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 5 wt-% $Al_2O_3$, and
0 to 10 wt-% additives.

5. Glasses or glass ceramics of any of the preceding claims with the following composition:
55 to 64 wt-% $SiO_2$,
10 to 20 wt-% $Li_2O$,
10 to 20 wt-% of a stabilizer selected from $ZrO_2$ and/or $HfO_2$,
0 to 5 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 5 wt-% $Al_2O_3$, and
0 to 10 wt-% additives.

6. Glasses or glass ceramics of any of the preceding claims with the following composition:
55 to 60 wt-% $SiO_2$,
10 to 20 wt-% $Li_2O$,
10 to 20 wt-% of a stabilizer selected from $ZrO_2$ and/or $HfO_2$,
0 to 5 wt-% $K_2O$ and/or $Na_2O$,
0,1 to 5 wt-% $Al_2O_3$, and
0 to 10 wt-% additives.

7. Glasses or glass ceramics of any of the preceding claims, characterised in that the stabilizer has substantially an amorphous structure.

8. Glasses or glass ceramics of any of the preceding claims, characterised in that the additives are selected from the group consisting of nucleating agents, fluorescent agents, dyes, preferably glass colouring oxides, coloured pigments and mixtures thereof.

9. Glasses or glass ceramics of claim 8, characterised in that the nucleating agents are selected from the group consisting of phosphorous oxide, titanium oxide, tin oxide, and mixtures thereof, and noble metals, preferably in an amount of 1 to 10 wt-%, more preferably 2 to 8 wt-% and most preferably 4 to 8 wt-%.

10. Glasses or glass ceramics of claim 8, characterised in that the fluorescent agents are selected from the group consisting of oxides of rare earth elements as neodymium, praseodymium, samarium, europium, terbium, dysprosium, holmium, erbium, and mixtures thereof, preferably in an amount of 0,1 to 5 wt-%, more preferably 0,5 to 4 wt-% and most preferably 1 to 3 wt-%.

11. Glasses or glass ceramics of claim 8, characterised in that the glass colouring oxides are selected from the group of oxides of iron, titanium, cerium, copper, chromium, cobalt, nickel, manganese, selenium, silver, indium, gold, vanadium, rare earth elements as neody-mium, praseodymium, samarium, europium, terbium, dysprosium, holmium, erbium, yttrium, and mixtures thereof, preferably in an amount of 0,1 to 6 wt-%, more preferably 0,5 to 5 wt-% and most preferably 1 to 4 wt-% and/or the coloured pigments are doped spinels, which are comprised preferably in an amount of 0,1 to 6 wt-%, more preferably 0,5 to 5 wt-% and most preferably 1 to 4 wt-%.

12. Glasses or glass ceramics of claim 8, characterised in that the additives are selected from the group consisting of boron oxide, fluorine, barium oxide, strontium oxide, magnesium oxide, zinc oxide, calcium oxide, yttrium oxide, titanium oxide, niobium oxide, tantalum oxide, lanthanum oxide and mixtures thereof,

preferably in an amount of 0,1 to 5 wt-%.

13. Method for producing a dental restoration comprising a lithium silicate glass or glass ceramic of any of the preceding claims, wherein

a) an glass is provided as starting material which comprises the components of the glass ceramic,

b) the glass is subjected to a first heat treatment for producing a glass ceramic which comprises lithium metasilicate as exclusive or main crystal phase,

c) the glass ceramic of b) is subjected to a second heat treatment, wherein further metasilicate is segregated from the glass phase and is existent as main crystal phase,

wherein the first heat treatment is effected with temperatures from 620 °C to 950 °C over a period of 1 to 200 min, preferably from 650 °C to 750 °C within a period of 10 to 60 min and/or the second heat treatment is effected with temperatures from 800 °C to 1040 °C over a period of 5 to 200 min, preferably from 800 °C to 870 °C within a period of 5 to 30 min.

14. Use of lithium silicate glasses or glass ceramics of any of claims 1 to 12 as a dental material or as a component of a dental material.

15. Shaped dental product comprising a lithium silicate glass or glass ceramic of any of the claims 1 to 12, preferably an inlay, an onlay, a bridge, an abutment, a facing, a veneer, a facet, a crown, a partial crown, a framework or a coping.

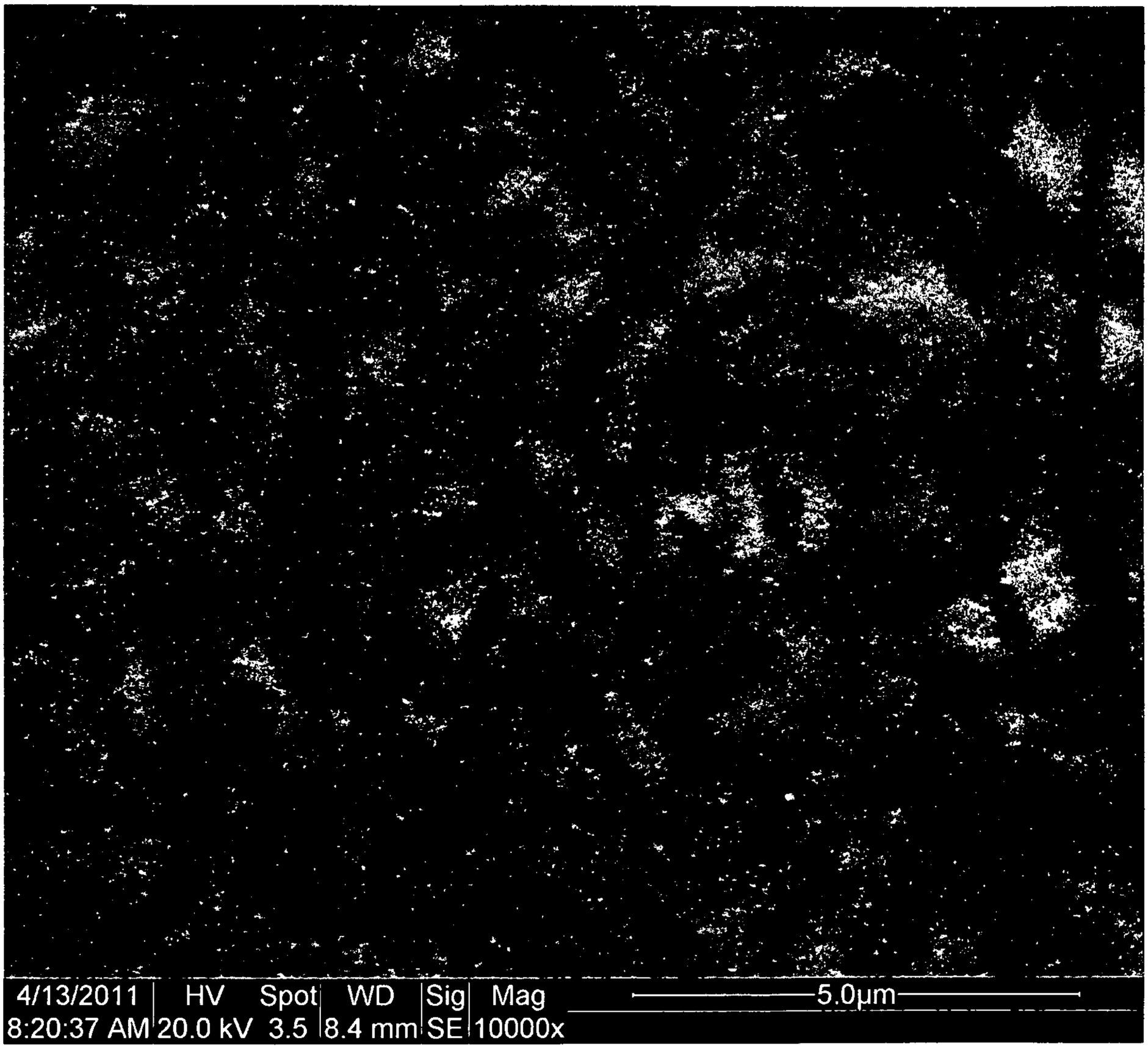
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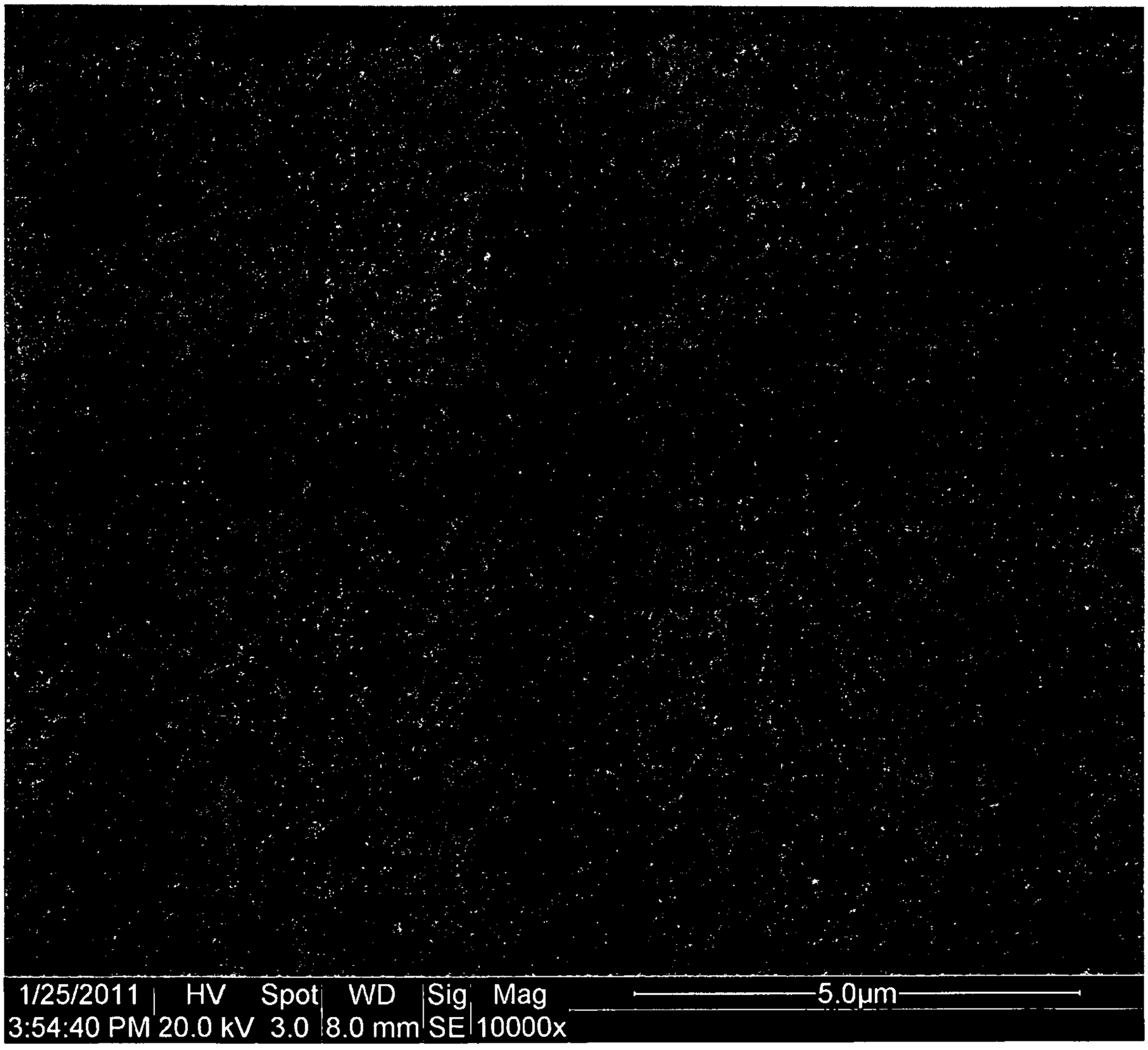
Fig. 1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5.0µm

Fig. 2

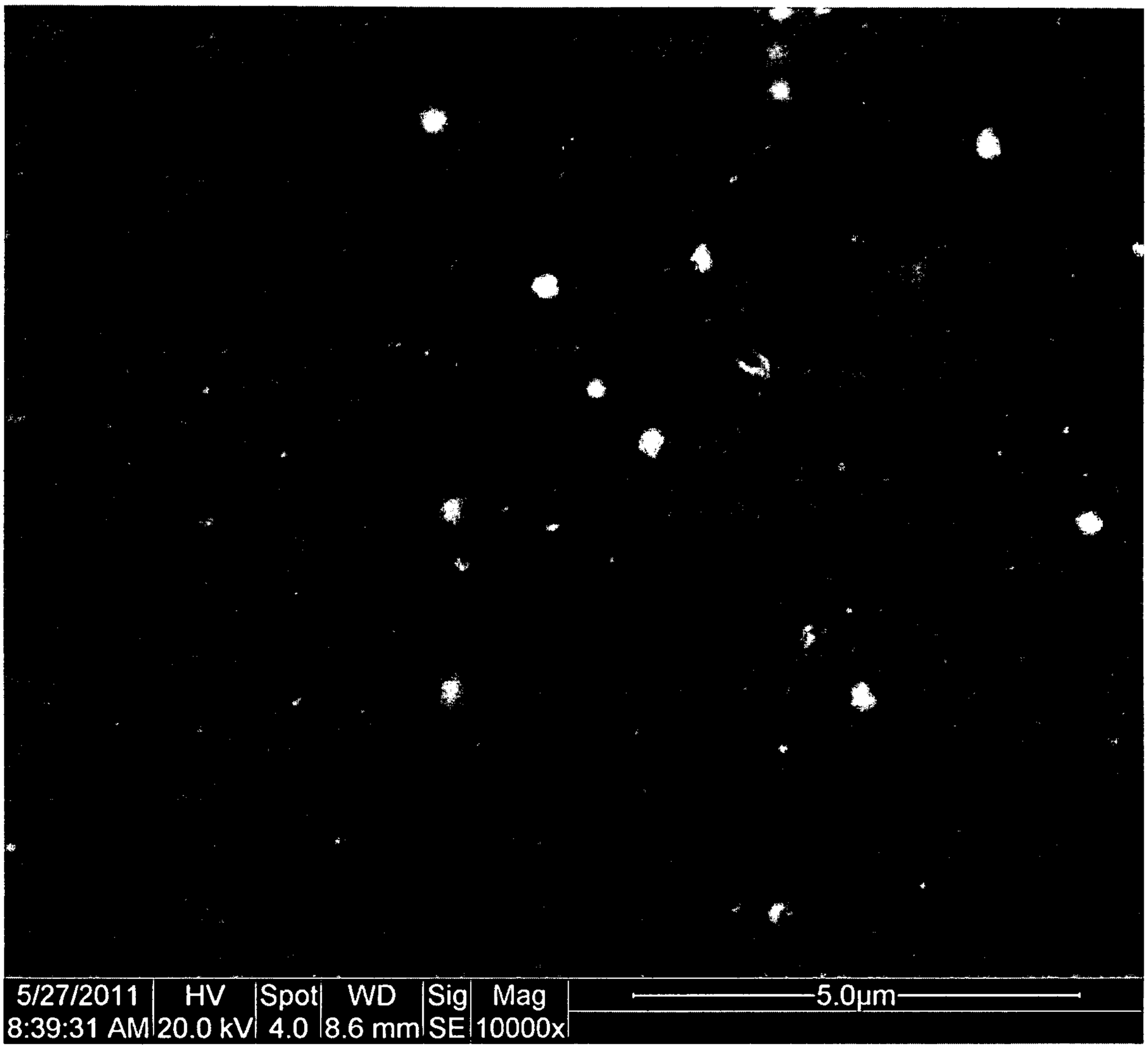
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Fig. 3