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(54) Title: SINTERED GLASS-CERAMIC MATERIAL PARTICULARLY SUITABLE AS A CLADDING AND STRUCTURAL SYSTEM (57) Abstract A sintered glass-ceramic material particularly suitable as a cladding and structural system, comprising a sintered ternary composition of SiO ₂ , LiO ₂ and ZrO ₂ which has an SiO ₂ /LiO ₂ molar ratio between 70/30 and 78/22 and a ZrO ₂ content of less than 13.04 mol.%. The glass-ceramic material according to the invention is used in the conventional field of ceramics and in the fields of screen-printing and lithography.		

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SINTERED GLASS-CERAMIC MATERIAL PARTICULARLY SUITABLE AS A CLADDING AND STRUCTURAL SYSTEM

Technical Field

The present invention relates to a sintered glass-ceramic material particularly suitable as a cladding and structural system.

5 In particular, the present invention relates to sintered glass-ceramic materials and composite materials with a glass-ceramic matrix, suitable for the cladding of structural elements and tiles of the ceramic type.

10 The starting material for producing the materials according to the invention is glass, i.e., an inorganic material which is amorphous due to the random arrangement of its structural units. This characteristic is made evident by the fact that in glass there is no exact melting point, which is instead typical of crystalline solids. In glassy systems, the basic structural unit is constituted by oxides, among which silicon oxide is the main component.

Background Art

Glass-ceramic materials, also known as glass-ceramics, are polycrystalline solid materials of the inorganic type which contain a residual amorphous phase.

20 The first techniques for preparing these materials were perfected by Corning Glass Works Limited in the USA and date back to 1947. These techniques entailed the transformation of a glassy material having a siliceous base into a polycrystalline ceramic material by providing a controlled thermal pretreatment for the nucleation of the glassy phase, followed by a so-called growth step.

25 Current methods for preparing simple and composite

glass-ceramic materials provide for suitable thermal treatments of glassy masses at a controlled temperature, usually in the presence of nucleating agents which facilitate the formation of the crystalline phase.

5 The present invention arises from the observation that there is strong market demand for new ceramic products suitable for cladding or structural application which meet the requirement of combining in a single product high functional properties with sophisticated aesthetic
10 qualities.

Disclosure of the Invention

 The aim of the present invention is to provide sintered glass-ceramic materials, particularly suitable as cladding and structural systems, which have, together with high surface hardness, good resistance to abrasion and are
15 also compatible with the main types of particulates and fibers used in the production of composites.

 An object of the present invention is to provide a method for producing sintered glass-ceramic materials whose execution uses technologies employed in the manufacture of
20 ceramic tiles, allowing low production costs.

 Another object is to provide a sintered glass-ceramic material which can be easily obtained starting from easily commercially available raw materials, has low porosity and high chemical durability, such as to make it particularly
25 suitable as a cladding or structural material for ceramic tiles.

 In view of this aim, these objects and others which will become apparent hereinafter, and according to a first aspect of the present invention, a sintered glass-ceramic

material is provided which is particularly suitable as a cladding and structural system which comprises a sintered ternary composition of SiO_2 , LiO_2 and ZrO_2 having an $\text{SiO}_2/\text{LiO}_2$ molar ratio between 70/30 and 78/22 and a ZrO_2 content of less than 13.04 mol%.

In accordance with a preferred embodiment, said material has a ZrO_2 content of 11.1 mol% or less.

In accordance with another aspect of the present invention, a method for preparing sintered glass-ceramic materials particularly suitable as cladding and structural systems is provided which comprises the steps of:

a) preparing a frit starting from a composition comprising SiO_2 , LiO_2 and ZrO_2 which advantageously has an $\text{SiO}_2/\text{LiO}_2$ molar ratio between 70/30 and 78/22 and a ZrO_2 content preferably of less than 13.04 mol%, more preferably less than 11.1 mol%;

b) breaking up the resulting frit to obtain a glassy powder;

c) pressing the resulting glassy powder into a compacted sample;

d) subjecting the resulting compacted sample to a heat treatment for sintering.

The raw materials suitable to form the frit, constituted by lithium carbonate, zirconium silicate and quartz, are easily commercially available at low cost in highly pure form (purity >99.5%).

The frit is advantageously prepared by grinding a starting material constituted by a ternary composition of SiO_2 , LiO_2 and ZrO_2 in which the $\text{SiO}_2/\text{LiO}_2$ molar ratio is between 70/30 and 78/22 and in which the ZrO_2 content is

lower than 13.04 mol%, until substantially spherical particles, with an average diameter of preferably less than 45 μm , are obtained. The ground particles are then melted to form an amorphous glassy mass which is cooled suddenly
5 with water or by contact with cold steel plates.

The frits are then broken up to yield a powdery glassy material with particles having an average diameter of preferably less than 100 μm ; this material is then advantageously ground to provide a glassy powder whose
10 granules have a diameter of preferably less than 2 mm.

The glassy powder produced by step b) is then subjected to a step for compaction by pressing with a conventional press, capable of developing pressures between 20 and 55 MPa.

15 The use of excessively coarse powders ($>100 \mu\text{m}$) does not ensure adequate sintering, while excessively fine powders, with an average diameter of 3 μm , have been found to be too reactive, facilitating the onset of secondary porosity, with a consequent degradation of the mechanical
20 properties of the final product.

It has been found that suitable sintering of the samples from step c) of the process according to the invention is provided by means of two alternative heat treatments.

25 The first one entails raising the temperature with a single heating ramp with a temperature increase gradient of 25 to 35 $^{\circ}\text{C}/\text{min}$ until temperatures between 600 and 980 $^{\circ}\text{C}$ are reached; this is followed by an isothermal treatment until a high degree of sintering is reached.

30 The second treatment entails, as an alternative, the

execution of a cycle with two heating ramps, both of which have a temperature increase gradient of 25 to 35 °C/min, separated by an isothermal period at a temperature in the interval between 700 and 800 °C and followed by isothermal
5 annealing at a temperature between 850 and 950 °C until a high degree of sintering is reached.

Sintered glass ceramics are used in conventional ceramics technology both as a protective cladding for ceramic tiles and as structural material in the manufacture
10 of ceramic tiles.

Comparative analysis with gres has further shown that the glass-ceramics produced with the process according to the invention have higher functional and aesthetic qualities. The characteristic milky coloring further allows
15 to color them easily by adding inorganic pigments during the preparation of the frits, allowing further dry or wet applications in screen-printing and/or lithographic methods.

In accordance with another aspect of the invention, a
20 process for producing decals particularly suitable for application to ceramic, glass and metal items is provided which comprises the steps of:

1) grinding a glass-ceramic frit according to the invention so as to obtain a glass-ceramic powder which
25 preferably has a residue of no more than 1% by weight at 15,000 mesh/cm² for wet grinding or of no more than 1% by weight at 10,000 mesh/cm² for dry grinding;

2) mixing the resulting powder with one or more colors and/or pigments to obtain a colored ceramic powder;

30 3) applying said colored ceramic mix to a decal

substrate by means of screen-printing or lithographic techniques to obtain a decal.

The decals produced according to this aspect of the invention are transferred onto items preferably made of ceramic, glass or metal by means of an annealing cycle (of
5 the rapid or semirapid type).

Within the frame of the present invention, said annealing cycle comprises a heat treatment at a temperature between 600 and 980°C, preferably at approximately 850°C,
10 advantageously for a period of time between 5 and 15 minutes, preferably 10 minutes.

The starting glass-ceramic frit can be in the form of a granulate and/or flakes, colorless (neutral) or colored; in the latter case, coloring is provided by melting with
15 colors or pigments.

The grinding step is advantageously performed in drum mills or cylindrical mills, preferably lined with high-density alumina and provided with alumina grinding media. Grinding can be performed dry or wet; in the latter case,
20 the resulting barbotine is dried with drying processes, among which vertical or horizontal atomization and continuous drying on a belt are preferred. The dried glass-ceramic material advantageously has a relative humidity of less than 0.5% by weight.

25 According to a particular aspect, the present invention relates to the above-described glass-ceramic powder obtained from the above-described grinding step and also to the mixture of said powder with colors and pigments.

30 The colors and pigments used during the coloring of

the ground product are of a type which is compatible with ceramic products, such as for example coloring oxides and ceramic colors.

5 The ceramic mix is applied to a suitable substrate for decals by means of screen-printing or lithographic techniques in predefined forms and in variable amounts in order to provide a decorative layer whose thickness is advantageously between 0.05 mm and 3 mm.

10 The decorative layer formed after the annealing cycle has a highly appreciable aesthetic effect and has class IV and V resistance to surface abrasion according to UNI EN 154 and IS 10545 standards. The decorative layer also provides high impermeabilization of the treated (decorated) surface, such as to allow classification in class V for
15 abraded surface stain resistance tests, according to the above-cited standards.

It has been found that the decorated surface is also highly resistant to thermal shock.

According to another aspect of the present invention,
20 a method is provided for the direct application of grit or powder of glass-ceramic material according to the invention to items by screen-printing or lithography, said method comprising the steps of:

25 1a) dry or wet grinding the glass-ceramic frit according to the invention to obtain a glass-ceramic grit or product which preferably has a residue of no more than 1% by weight at 15,000 mesh/cm² for wet grinding and a residue at 10,000 mesh/cm² for dry grinding, said wet-ground product being then dried, or, as an alternative,

30 1b) granulating the glass-ceramic frit according to

the invention to obtain a glass-ceramic grit,

2) optionally mixing said glass-ceramic ground product or grit with a color or pigment, conveniently in the presence of a suitable fluidifying and/or agglomerating
5 vehicle;

3) applying the glass-ceramic ground product or grit, either neutral or colored by screen-printing or lithography, directly to an item, to provide a decorative surface layer; and, advantageously,

10 4) subjecting to an annealing cycle.

The method according to the present aspect of the invention allows to provide, on the surface of the item, one or more layers based on sintered glass-ceramic material, which in addition to being highly resistant to
15 wear and abrasions produces a decorative and chromatic effect which is highly appreciable from an aesthetic point of view.

This method gives the treat item a high added value.

The starting glass-ceramic material can be in the form
20 of a granulate or flakes, colorless (neutral) or colored; in the latter case, coloring is provided by melting with colors or pigments.

Advantageously, the grinding step is performed in mills of the above-described type.

25 The colors or pigments used to color the glass-ceramic ground product or grit are of the type commonly used in the ceramics field. These colors/pigments are added in such an amount as to provide a coloring which is detectable by the human eye and is conveniently between 0.1% and 10% by
30 weight with respect to the glass-ceramic material.

Advantageously, carriers, diluents and additives commonly used in screen-printing and/or lithographic application methods are added during mixing.

According to a particular aspect, the present invention further relates to the ground product and to the grit made of glass-ceramic material, obtained during step 1) of the process, according to this last aspect of the invention, and to the mixture of said ground product or grit with colors or pigments according to step 2) of the process.

According to yet another aspect of the present invention, a process for producing items with a glass-ceramic base is provided which comprises the steps of:

1) grinding the glass-ceramic frit according to the invention to obtain a glass-ceramic powder which preferably has a residue of no more than 1% by weight at 15,000 mesh/cm² when wet grinding is performed, or a residue of no more than 1% by weight at 10,000 mesh/cm² when dry grinding is performed;

2) adding, if necessary, an amount of water to obtain a semifluid mix suitable to a forming process;

3) subjecting the mix to a forming process;

4) subjecting to an annealing cycle.

Within the frame of this aspect of the invention, the term "forming" relates to a conventional forming process, preferably selected from casting, forming in the plastic state (plastic forming) and forming in the semi-dry state (semi-dry forming).

If step 1) of the process entails wet grinding, a barbotine which conveniently includes 30 to 40% water is

obtained.

According to an embodiment, the barbotine obtained from wet grinding is poured to obtain a wet semifinished item which is dried and then annealed. The resulting item
5 is made of sintered glass-ceramic material.

According to another embodiment, the barbotine obtained from wet grinding is dried, for example by using vertical or horizontal atomizers. The drying process provides a granulate which conveniently contains 4 to 6%
10 water and preferably has an average particle size between 50 and 450 microns.

Said granulate can be worked with two operating methods.

The first method provides for molding in the semi-dry
15 state (4-6% relative humidity), in which the granulate is pressed to obtain a semifinished item, for example a tile, plate or other shape. The resulting semifinished item is then dried and annealed.

The second operating method entails subjecting the
20 granulate, after adding water, to plastic forming by means of at least one drawing and cutting process; once the intended shape has been obtained, optionally by additional pressing, the item is dried. The dried item is then sent to the furnace for annealing.

25 When step 1) of the process provides for dry grinding, a glass-ceramic powder is obtained to which water is added to provide a mix which is suitable for forming according to one of the following methods: casting, molding in the plastic state and molding in the semi-dry state.

30 In particular, it has been found that by adding an

amount of water equal to 30-40% by weight with respect to the weight of the dry glass-ceramic powder, a semifluid mix is obtained which is suitable for casting; by adding an amount of water equal to 15-20% by weight with respect to the weight of the dry glass-ceramic powder, a mix is obtained which is suitable for plastic forming; by adding an amount of water equal to 4-6% by weight with respect to the weight of the dry glass-ceramic powder, a mix is obtained which is suitable for molding in the semi-dry state.

Conveniently, the added water contains fluidifiers, suspension promoters and additives which are suitable to give the mix the optimum physical characteristics for forming.

When forming step 3) of the process provides for the casting of the semifluid mix, the resulting semifinished item, generally after a finishing step, is sent directly to steps 4) and 5) for drying and furnace annealing.

Vice-versa, when said step 3) provides for plastic forming of the mix, a semifinished item is obtained which can be pressed or extruded. The resulting semifinished item is then rolled, cut, optionally pressed and finished before being dried and annealed.

If said step 3) provides for the molding in the semi-dry state of the mix, a semifinished item having a specific shape is produced which can then be sent to the drying and annealing steps.

The items obtained at the end of the process according to this aspect of the invention can be decorated by applying thereon the decals of the above-described type by

means of screen-printing or lithographic methods.

Items produced in accordance with this aspect of the invention have a high resistance to surface abrasion, in class V and higher according to UNI EN 154 and ISO 10545 standards; a deep abrasion resistance which meets the requirements of the UNI EN 176 standard; a high impermeabilization of the surface, such as to allow to classify them in class V in the abraded surface stain resistance test, according to the above-cited standards; and a high resistance to thermal shock.

Within the scope of the present invention, the above-described techniques for applying the sintered glass-ceramic material to items are of a known type, as disclosed in EP 0 570 855, or are lithographic and screen-printing techniques used in the field of the working/decoration of ceramic items, such as for example those disclosed in EP 0 769 372 and EP 0 805 131. The above-cited patents are assumed to be entirely included herein as reference.

The following examples are given merely to illustrate the present invention and must not be considered as limiting the scope of said invention as defined in the appended claims.

EXAMPLE 1

Preliminary step - Preparation of the glassy systems

The glassy systems that are suitable for producing the materials according to the invention were prepared by using, as raw materials, lithium carbonate (Li_2CO_3), quartz

(SiO_2) and zirconium silicate (ZrSiO_4) of high purity (>99.5%) and with an average particle diameter of less than 45 μm .

The initial powders were homogenized by means of a mixer until compositions selected in terms of $\text{SiO}_2/\text{LiO}_2$ ratio and zirconium oxide content were obtained, as listed in table 1. The maximum allowed ZrO_2 was 13.04 mol% (over this content it has been found that regardless of the values of the $\text{SiO}_2/\text{LiO}_2$ molar ratios, incomplete dissolution of ZrSiO_4 in the glassy structure was observed).

The initial material used is constituted by raw materials which are commonly commercially available and are currently used in the preparation of ceramic enamels.

Table 1 below lists the chemical compositions, in mol%, of the vitreous systems that have been found to be particularly suitable for forming the frits of step a) of the process according to the invention.

Composition	O x i d e s (mol %)	
	SiO ₂ /Li ₂ O	ZrO ₂
A1	70/30	-
A2		2.44
A3		4.76
A4		6.98
A5		9.10
A6		11.10
A7		13.04
B1	74/26	-
B2		6.98
B3		9.10
B4		11.10
B5		13.04
C1	76/24	-
C2		6.98
C3		9.10
C4		11.10
C5		13.04
D1	78/22	-
D2		6.98
D3		9.10
D4		11.10
D5		13.04

An amount of each composition sufficient to produce approximately 100 g of vitreous system was dry-homogenized and then transferred into a metallic crucible to be subjected to a heat treatment lasting a total of
5 approximately 7 hours in an electric furnace preset to reach maximum temperatures between 1400 and 1500 °C (depending on the ZrO_2 content). At these temperature values one obtains sufficient fluidity and homogenization of the components of the molten substance and the complete
10 dissolution of ZrSiO_4 in the glassy structure. The resulting homogeneous glassy system was cooled by casting into water and/or onto a stainless steel plate.

The glassy system was divided into 10-g samples, which were cooled, dried and dry-ground in a mill for
15 approximately 40 minutes. The result was a powder constituted by substantially spherical particles with a diameter of less than 20 μm for X-ray diffraction on powders (XRD), differential thermal analysis (DTA), FT-IR spectroscopy and for the preparation of the specimens to be
20 subjected to preliminary sintering tests.

Step a): Preparation of the frits

The initial step of the method according to the invention consists in preparing the frits, which allow to obtain a glassy powder which, compacted by pressing, can be subjected to a suitable sintering treatment.

25 Compositions having $\text{SiO}_2/\text{LiO}_2$ molar ratios equal to 70/30, 72/26, 76/24 and 78/22 with 11.10 mol% of ZrO_2 always have high-level transparency characteristics,

together with good mechanical properties and good stability from the chemical point of view. These compositions have been found to crystallize easily and to be accordingly also particularly suitable for obtaining glass-ceramic and/or
5 composite materials even with rather bland heat cycles.

The selected compositions according to the invention were prepared starting from lithium carbonate (Li_2CO_3), zirconium silicate (ZrSiO_4) and quartz (SiO_2); these starting components had a high purity ($>99.5\%$) and an
10 average particle diameter of less than $45\text{ }\mu\text{m}$.

Table 2 below lists the percentages by weight of the constituent oxides of the raw materials used in the preferred compositions.

Composition	Li ₂ O (wt %)	ZrO ₂ (wt %)	SiO ₂ (wt %)
A6	13.50	23.17	63.33
B4	11.49	22.77	65.74
D4	9.56	22.36	68.08

An amount equal to 2 kg for each selected composition was subjected to dry mixing in a ball mill and then transferred to a gas-fired furnace, where they melted at a temperature of approximately 1500 °C after a heat cycle
5 lasting 7 hours.

The resulting glassy system was then cooled suddenly by casting into water.

Step b): Preparation of the glassy powders

The frits produced in step a), after drying in a stove, were subjected to a dry breakup treatment in a
10 ceramic vessel until a glassy powder with an average diameter of less than 100 µm was obtained.

In order to achieve a further reduction in particle size, the glassy powder was advantageously subjected to wet grinding in a discontinuous rotary cylindrical mill in the
15 presence of grinding media made of sintered alumina, using barbotines with a density of 1.6 g/cm³.

During wet grinding, samples of the barbotine were taken at regular time intervals in order to measure and check particle size distribution.

20 The maximum wet grinding time was programmed to 72 hours.

The suspension was dried in a stove at 110 °C until a constant weight was reached.

The powders were then disaggregated in a ceramic
25 vessel and then humidified, adding water in an amount equal to 6% by weight, without introducing any binder in the resulting mix.

In order to achieve a more effective compaction of the unfired material, granulation was performed in a cylindrical container for 4-6 minutes, obtaining substantially spherical granules with an average diameter of less than 2 mm.

Step c): Compaction

The powders, granulated as described in step b), were then compacted uniaxially by using a press capable of developing a working pressure of 40 MPa (400 bar). Following compaction, samples with different formats were produced:

- samples shaped like parallelepipeds with nominal dimensions of 7 x 50 x 100 mm to be subjected to deep abrasion tests;

- cylindrical samples with a nominal diameter and height of 13 mm and 6 mm, respectively, to be subjected to preliminary characterization tests and to X-ray analysis;

- samples shaped like a parallelepiped with nominal dimensions of 7 x 20 x 50 mm to be subjected to mechanical, thermal, chemical and structural tests.

Step d) - Sintering

The pressed and stove-dried samples were then subjected to the thermal treatment for sintering, which was performed by annealing in a gradient furnace in an oxidizing atmosphere at temperatures between 600 and 980 °C, more preferably between 750 and 800 °C. The samples

were then left to cool until ambient temperature was reached.

In order to reach high degrees of sintering, two alternative types of heat cycle were used, and the first one yielded more satisfactory results:

1) a cycle performed with a single heating ramp of 30°C/min, followed by isothermal annealing for 10-60 minutes;

2) a cycle performed with two heating ramps, both of 30°C/min, separated by an isothermal interval at 750 °C lasting 10 minutes, followed by an isothermal annealing step at 900 °C lasting 10 minutes.

The best results in terms of degree of sintering were achieved with a heating ramp of 30°C/min, until a temperature of 900 °C was reached, and performing a subsequent isothermal annealing for 10 minutes.

EXAMPLE 2

Comparison between the properties of glass ceramics according to the invention and those of some ceramic-type materials of the prior art.

The glass-ceramic materials sintered with the process according to the invention have improved characteristic properties when compared with materials of the prior art.

Specifically, the modulus of rupture of the glass-ceramic material was found to be 3 times higher than for a porcelainized gres. This characteristic is of particular value if the glass-ceramic materials according to the

invention are used in the production or cladding of tiles, since a distinct reduction in thickness, and therefore in mass is achieved while maintaining structural values unchanged.

5 The main properties of the glass-ceramic materials produced with the process according to the invention, characterized by a step for sintering at 900 °C for 10 minutes, are listed below in table 3, which is provided merely by way of example and in which: M = white and
10 colored marble; G = granite; NP = Neoparies; GP = porcelainized gres.

Table 3

Properties	A6	B4	D4	M	G	NP	GP
Apparent density (g/cm ³)	2.61	2.61	2.65	† 2.69 † 2.69 (2.70)	2.64 (2.60)	(2.70)	2.37 (<2.70)
Total porosity (%)	11.6	11.2	8.8	-	-	-	(6-7)
Water absorption (%)	<0.01	<0.01	<0.01	-	-	(<1)	(<1)
ChrySTALLINITY (%)	51.6	53.5	55.9	-	-	(40.0)	(<40.0)
Elastic modulus (GPa)	113±2.4	111±1.6	107±1.2	†41±8 †68±0.3 (27-82)	58±1 (42-60)	(51)	66±5 (65-72)
Poisson's ratio (-)	0.19	0.17	0.16	-	-	-	-
Modulus of rupture (MPa)	149±10	157±7	163±9	†14±4 †16±1 (16.7)	27±5 (14.7)	(50)	73±6 (45-60)
Microhardness (GPa)	5.67±0.2	5.75±0.4	6.05±0.4	-	-	-	(4.9-6.10)
Deep abrasion value (mm ³)	34	34	35	†650±15 †609±36	142±1	-	135±4 (120-150)
Thermal expansion coefficient (10 ⁻⁶ °C ⁻¹)	10.3	10.2	10.0	†19.0 †12.5	19.8	-	8.3 (7-9)
Chemical resistance							
Acids (%)	0.06	<0.01	<0.01	(10.30) †5.74 †5.83 (0.30)	(1.00) 0.15 (0.10) 0.03	(0.08)	0.01
Bases (%)	0.36	0.09	<0.01	†8.99 †0.005		(0.05)	0.03

The glassy system used in the present invention reaches, at temperatures in the range between 750-800 °C and when performing heat cycles with a total duration of 40 minutes, densification above 90% without the onset of shape
5 distortions in the material.

Qualitative and quantitative analysis of the crystalline phases of the materials according to the invention has revealed the formation, at temperatures above 850 °C, of lithium disilicate and zirconium silicate and
10 the absence of cristobalite.

It has been found that total crystallinity at 900 °C is close to values between 50 and 55% by weight, rising to 60% at 950 °C; it has been found that an excessive growth of the particles occurs at the latter temperature,
15 consequently forming secondary porosity which degrades the degree of densification of the material.

An analysis of micrographs shows that the composition designated earlier as D4 has a microstructure which is characterized by crystals which are slightly finer than
20 those of composition A6.

It has also been noted that the glass-ceramic materials according to the invention have mechanical properties which are optimized at 900 °C.

This temperature is an intermediate value between the
25 temperatures of 750-800 °C at which the maximum degree of densification is reached and the temperatures of 900-950 °C at which complete crystallization occurs.

The materials obtained by sintering starting from compositions A6, B4, D4 have shown values of the modulus of
30 rupture of more than 160 MPa, a Vickers hardness of

approximately 6 GPa, an elastic modulus of approximately 110 GPa and a deep abrasion value of approximately 34 mm³. These values are distinctly different from those obtained by analyzing samples of known kinds of ceramic material.

5 In particular, D4, the composition that is richest in silica, has shown better microstructural characteristics than compositions B4 and A6.

10 Further advantages related to the use of the glass-ceramic materials according to the invention are evident by examining the values of the thermal expansion coefficient, which for composition D4 at 900°C reach $10 \cdot 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, while chemical durability values have shown practically nonexistent weight losses following acid and basic attack.

15 The properties of the glass-ceramic materials according to the invention have values which are typical of advanced ceramics although they are produced with heat treatment methods which are typical of conventional ceramics.

20 Additionally, by virtue of their high aesthetic, structural and surface qualities they can be used as a cladding for porous structural materials or as external claddings instead of marble.

25 The disclosures in Italian Patent Application No. MI98A000414 from which this application claims priority are incorporated herein by reference.

CLAIMS

1 1. A sintered glass-ceramic material, particularly
2 suitable as a cladding and structural system, characterized
3 in that it comprises a sintered ternary composition
4 comprising SiO_2 , LiO_2 and ZrO_2 which has an $\text{SiO}_2/\text{LiO}_2$ molar
5 ratio between 70/30 and 78/22 and a ZrO_2 content of less
6 than 13.04 mol%.

1 2. A material according to claim 1, characterized in
2 that it has a ZrO_2 content of 11.1 mol% or less.

1 3. A method for preparing a sintered glass-ceramic
2 material, particularly suitable as a cladding and
3 structural system, characterized in that it comprises the
4 steps of:

5 a) preparing a frit starting from a ternary
6 composition of SiO_2 , LiO_2 and ZrO_2 which has an $\text{SiO}_2/\text{LiO}_2$
7 molar ratio between 70/30 and 78/22 and a ZrO_2 content of
8 less than 13.04 mol%;

9 b) breaking up the resulting frit to obtain a glassy
10 powder;

11 c) pressing the resulting glassy powder into a
12 compacted sample;

13 d) subjecting the resulting compacted sample to a heat
14 treatment for sintering.

1 4. A method according to claim 3, characterized in
2 that the initial frit has a ZrO_2 content equal to, or lower
3 than, 11.1 mol%.

1 5. A method according to claim 3 or 4, characterized
2 in that said frit is prepared by grinding a starting
3 material which comprises lithium carbonate, zirconium

4 silicate and quartz until a powdery mix is obtained in
5 which the particles have an average diameter of less than
6 45 μm ; subjecting said powdery mix to a thermal treatment
7 for melting until a molten mass is obtained; and then
8 suddenly cooling said glassy mass.

1 6. A method according to any one of claims 3-5,
2 characterized in that the step b) for breaking up the frit
3 comprises a preliminary breakup treatment to yield a glassy
4 powder whose particles have an average diameter of less
5 than 100 μm and a granulation to obtain a granulated powder
6 in which the granules have a diameter of less than 2 mm.

1 7. A method according to any one of claims 3-6,
2 characterized in that the pressing step c) comprises the
3 compaction of the glassy powders at a pressure between 20
4 and 55 MPa.

1 8. A method according to any one of claims 3-7,
2 characterized in that the sintering step d) comprises a
3 cycle with a single heating ramp of 25-35 $^{\circ}\text{C}/\text{min}$ to reach
4 temperatures between 600 and 980 $^{\circ}\text{C}$ and a subsequent
5 isothermal annealing.

1 9. A method according to claim 8, characterized in
2 that said heating ramp is of 30 $^{\circ}\text{C}/\text{min}$ and said isothermal
3 annealing lasts 10-60 minutes.

1 10. A method according to any one of claims 3-9,
2 characterized in that during said step a) at least one
3 organic pigment is added to provide a colored frit.

1 11. Use of a glass-ceramic material according to claim
2 1 or 2 as protective cladding for ceramic tiles.

1 12. Use of a glass-ceramic material according to claim
2 1 or 2 as a structural component for ceramic tiles.

1 13. Use of a glass-ceramic material according to
2 claims 1 or 2 in screen printing.

1 14. Use of a glass-ceramic material according to
2 claims 1 or 2 in lithography.

1 15. A method for preparing a glass-ceramic frit which
2 comprises the steps of:

3 -- grinding a starting glassy material which comprises
4 a ternary composition of SiO_2 , LiO_2 and ZrO_2 in which the
5 $\text{SiO}_2/\text{LiO}_2$ molar ratio is between 70/30 and 78/22 and in
6 which the ZrO_2 content is lower than 13.04 mol%, in order
7 to obtain a glassy ground material;

8 -- melting said ground material to produce an
9 amorphous glassy mass and then

10 -- cooling.

1 16. A method for producing decals particularly
2 suitable for application to ceramic, glass and metal items,
3 comprising the steps of:

4 1) dry- or wet-grinding a glass-ceramic frit according
5 to claim 15 so as to obtain a glass-ceramic powder;

6 2) mixing the resulting powder with one or more colors
7 and/or pigments to obtain a colored ceramic powder;

8 3) applying said colored ceramic mix to a decal
9 substrate by means of screen-printing or lithographic
10 techniques.

1 17. A method according to claim 16, characterized in
2 that the glass-ceramic powder obtained from the grinding
3 step 1) has a residue of no more than 1% by weight at
4 15,000 mesh/cm² for wet grinding and a residue of no more
5 than 1% by weight at 10,000 mesh/cm² for dry grinding.

1 18. A method for the direct application of grits or

2 powders of glass-ceramic material to items by screen-
3 printing or lithography, said method comprising the steps
4 of:

5 -- dry- or wet-grinding or granulating the glass-
6 ceramic frit according to claim 15 in order to obtain a
7 glass-ceramic ground product or grit;

8 -- applying said glass-ceramic ground product or grit
9 directly onto an item by screen-printing or lithography so
10 as to provide a decorative surface layer; and then

11 -- subjecting to an annealing cycle.

1 19. A method according to claim 18, further comprising
2 an intermediate step for mixing said glass-ceramic ground
3 product or grit with a color or a pigment, before
4 application to the item.

1 20. A method for manufacturing items having a glass-
2 ceramic base, comprising the steps of:

3 1) grinding the glass-ceramic frit according to claim
4 15, in order to obtain a glass-ceramic powder;

5 2) subjecting the powder to forming;

6 3) subjecting the formed powder to an annealing cycle.

7 21. A method according to claim 20, further comprising
8 the addition of water to the glass-ceramic powder of step
9 1) before subjecting to forming.

1 22. A method according to claim 20, characterized in
2 that said forming is molding in the plastic state, molding
3 in the semidry state or molding by casting.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01323

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C10/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

DOSYS EUREG

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEKHOVSKII V G ET AL: "CRYSTALLIZATION OF LITHIUM ZIRCONIUM SILICATE GLASSES" SOVIET JOURNAL OF GLASS PHYSICS AND CHEMISTRY, vol. 15, no. 3, 1 May 1989 (1989-05-01), pages 265-272, XP000121248 ISSN: 0360-5043 the whole document ---	1-22
X	OLIVEIRA DE A P N ET AL: "SINTERING AND CRYSTALLIZATION OF A GLASS POWDER IN THE LI2O-ZR02- SiO2 SYSTEM" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol. 81, no. 3, 1 March 1998 (1998-03-01), pages 777-780, XP000738310 ISSN: 0002-7820 the whole document --- -/--	1-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

13 July 1999

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01323

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NOVAES DE OLIVEIRA ANTONIO PEDRO ET AL: "Physical properties of quenched glasses in the Li ₂ O-ZrO ₂ -SiO ₂ system" J AM CERAM SOC; JOURNAL OF THE AMERICAN CERAMIC SOCIETY APR 1996 AMERICAN CERAMIC SOC, WESTERVILLE, OH, USA, vol. 79, no. 4, April 1996 (1996-04), pages 1092-1094, XP002108890 the whole document	1-22
X	--- P. QUINTANA ET AL.: "Preliminary Study of the System Li ₂ O-ZrO ₂ -SiO ₂ " TRANSACTIONS OF THE BRITISH CERAMIC SOCIETY., vol. 80, no. 3, 1981, pages 91-96, XP002108891 BRITISH CERAMIC SOCIETY. STOKE-ON-TRENT., GB page 91 page 93 page 95	1-22
X	--- CHEMICAL ABSTRACTS, vol. 70, no. 12, 24 March 1969 (1969-03-24) Columbus, Ohio, US; abstract no. 50081, E. M. MILYUKOV: "Crystallization and structure of lithium zirconium silicate glasses" XP002108893 abstract & ZH. PRIKL. KHIM., vol. 41, no. 12, 1968, pages 2614-2618, Leningrad	1-22
P, X	--- A. P NOVAES DE OLIVEIRA ET AL.: "Properties of glasses belonging to the Li ₂ O-ZrO ₂ -SiO ₂ system" PHYSICS AND CHEMISTRY OF GLASSES., vol. 39, no. 4, August 1998 (1998-08), pages 213-221, XP002108892 SOCIETY OF GLASS TECHNOLOGY. SHEFFIELD., GB ISSN: 0031-9090 page 213 - page 214 -----	1-22