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(54) Title: CERAMIC DENTAL RESTORATION MATERIAL

(57) Abstract: A ceramic dental restoration material having a composition comprising: a diopside crystalline phase and a leucite crystalline phase, both of which may be dispersed in a feldspathic glassy matrix. Also disclosed is a method of making the same and use of the same.

Ceramic Dental Restoration Material

The present invention relates to a ceramic dental restoration material, to a method of making such a material, and to use of such a material in restorative dentistry. In particular, the present invention relates to a ceramic dental restoration material having a multiple phase structure, to a method of making the same, and to use of the same in dentistry, especially aesthetic restorative dentistry.

Aesthetic leucite-feldspar ceramic veneers have been widely used in dentistry for many years. They are used in metal-ceramic restorations, i.e. restorations based upon a metallic core on which a ceramic veneer is applied, for ceramic restorations which are based on a high strength ceramic core, and/or can be resin-bonded to the enamel and/or dentine of an existing tooth. Restorations include both anterior and posterior crowns, veneers, onlays and inlays. Together leucite (otherwise known as potassium aluminium tectosilicate: $K[AlSi_2O_6]$) and feldspar (belonging to a group of tectosilicate minerals comprising: $K[AlSi_3O_8]$, $Na[AlSi_3O_8]$ and $Ca[AlSi_3O_8]_2$) form glass-ceramic compositions having many desirable properties, including strength, hardness, linear coefficient of thermal expansion and good optical properties.

A number of leucite-feldspar ceramic dental restorations are described in the art; more specifically two-phase materials comprising a leucite crystalline phase dispersed in a glassy feldspathic matrix are known. Table I overleaf illustrates a number of known veneering “systems”, i.e. it describes known combinations of core materials and compatible veneering ceramics.

Despite the prevalence of such leucite crystallite-containing glass-ceramics in both the prior art and currently in use in dentistry practice, there are still numerous problems associated with these types of glass-ceramics, which it would be desirable to overcome. One of the most common problems is failure of a such a ceramic composition due to the presence of cracks or micro-defects within the ceramic, leading to exposure of the underlying core material (be that a metal core or a ceramic core) and thus a failed restoration.

Table I

System	Core		Veneer	
	Material	Coefficient of Thermal Expansion (ppm/°C)	Material	Coefficient of Thermal Expansion (ppm/°C)
metal	metal alloy	13.8-15 (at 25-500 °C)	(a) high leucite-content glass ceramic, e.g. IPS Classic, or (b) leucite-apatite glass ceramic, e.g. IPS d.sign	(a) 12.6-13.2 (b) 12.0-12.6
titanium	titanium	9.6 (at 25-500 °C)	VITA titanium ceramic	8.2-8.9
VITA In-Ceram® Alumina	alumina-infiltrated glass	7.2-7.6 (at 25-500 °C)	feldspathic glass e.g. VITA VM7	6.9-7.3
VITA In-Ceram® Spinel	magnesium spinel-infiltrated glass	7.5-7.9 (at 25-500 °C)	feldspathic glass e.g. VITA VM7	6.9-7.3
VITA In-Ceram® Zirconia	partially stabilised zirconia (35 %)-infiltrated glass	7.6-7.8 (at 25-500 °C)	feldspathic glass e.g. VITA VM7	6.9-7.3
VITA In-Ceram® AL	pure aluminium oxide	7.3 (at 25-500 °C)	feldspathic glass e.g. VITA VM7	6.9-7.3
VITA In-Ceram® YZ	zirconium dioxide partially stabilised with yttrium oxide	10.5 (at 25-500 °C)	leucite-feldspathic glass e.g. VITA VM9	9.5
IPS e.max	lithium disilicate glass	10.5 (at 100-500 °C)	fluorapatite glass e.g. IPS e.max ceram	9.5

As such, there are a number of desirable qualities for a dental ceramic composition, including exhibition of pleasing aesthetics to enable matching to a range of tooth shades, including colour stability, translucency (that is similar in range to that of enamel and dentine) and surface finish, possession of a minimum level of abrasion resistance, inherent strength and toughness, tissue compatibility, chemical stability, and, in the case of application to an artificial core material (i.e. a metallic core or a ceramic core), ideally have a coefficient of thermal expansion which is as closely matched as possible to the underlying core material to which the ceramic composition is applied to minimise any effects of thermal shock during preparation of the restoration.

A non-optimised composition can lead to brittle fracture of the ceramic, which involves the rapid, uninterrupted propagation of cracks, usually beginning at a flaw in the ceramic itself, and also increases the risk of abrasive wear of surrounding, and particularly opposing, tooth structure(s). Furthermore, once *in situ*, a restoration formed from a non-optimised composition may undesirably fracture and/or easily chip.

Typically full ceramic restorations are preferred over metal-ceramic restorations because of the inherent shrinkage (and consequential poor fit) that often occurs due to a mis-match in linear coefficient of thermal expansion between the metal core and the applied ceramic, the reduced light transmission through a metal-ceramic restoration (making the restoration appear undesirably darkened as compared to the surrounding teeth), discolouration of the ceramic due to metal-ion migration from the metal core and possible allergic reaction to the metal core. The preferred full ceramic restorations must however possess the necessary mechanical strength to properly function.

The process for manufacturing high strength full ceramic restorations can involve many firing cycles (unless other formation processes such as hot-pressing or computer-aided design and computer-aided manufacturing (CAD-CAM) are used). During the heating and cooling cycles, ceramics change in length and volume, and as such it is important that the core and veneering ceramic are thermally compatible to prevent thermal stress formation in restorations during ceramic processing, otherwise this may lead to crazing, cracking, delamination or fracture and contribute to the failure of the restorations. Unfortunately, such failures are still too often observed.

It would therefore be desirable to produce a ceramic dental restoration composition which does not suffer from the problems outlined above, or at least the effect of these problems are minimised insofar as is possible, which exist despite the wealth of teaching that clearly exists in this field.

Accordingly, in a first aspect, the present invention provides a ceramic dental restoration material having a composition a diopside crystalline phase and a leucite crystalline phase, preferably forming a dual crystalline phase structure. Surprisingly, such a composition appears to be particularly compatible with precious metal alloy cores, e.g. dental gold alloy cores, such that the aforementioned benefits are achievable, as will be discussed in more detail below.

Said diopside-crystalline phase and leucite-crystalline phase containing composition according to the first aspect of the invention may yet further comprise a feldspathic glassy matrix having both the leucite crystalline phase and the diopside crystalline phase dispersed therein.

The feldspathic glassy matrix is typically an amorphous phase in which each of the leucite and diopside crystalline phases are dispersed, which is determinable by both x-ray diffraction (XRD) and scanning electron microscopy (SEM).

Such ceramic dental restoration materials are advantageous over known restoration compositions because they all possess the desirable features of pleasing aesthetics, (colour stability, translucency and surface finish), excellent inherent strength and toughness, good abrasion resistance, tissue compatibility, chemical stability, and has a coefficient of thermal expansion which closely matches an underlying core material, as will be described in more detail below.

Of course, a person skilled in the art will appreciate that, where a ceramic dental restoration material according to the invention is to be resin-bonded to the enamel and/or dentine of an existing tooth (rather than applied to a metallic or ceramic core), the coefficient of thermal expansion of the restoration material is irrelevant. However, instead, the restoration material must be (and is believed to be) compatible with resin technologies commonly used in dentistry. In this regard, the ceramic dental restoration material of the invention is preferably treatable with silane, prior to being resin-bonded.

Preferably the composition of the invention may be formed from the following combinations of glass frits:

10 to 40 % by weight (preferably 10 to 22 %) of a diopside glass frit
50 to 80 % by weight (preferably 58 to 70 %) of a leucite glass frit
5 to 25 % by weight (preferably 10 to 20 %) of a feldspar glass frit

with the proviso that the sum total amount of the glass frits is at least 80-100 %, with the remaining 0-20 % being one or more other ingredients included in the composition.

Further preferably, the sum total of the glass frits in said composition is 100 %.

Inclusion of a leucite crystalline phase in the ceramic restoration material of the invention is particularly advantageous because it acts to control the coefficient of thermal expansion of the material and the translucency of the material, and it can improve the inherent strength of the material.

As discussed above, the composition of the invention may further comprise one or more ingredients, which may comprise any one or more oxides of the following: titanium (e.g. TiO_2), cerium (e.g. CeO_2), tin (e.g. SnO_2) and vanadium (e.g. V_2O_5) in a total amount of from 0 to 20 % by weight, preferably from 0.0001 to 10 % by weight and more preferably from 0.0005 to 5% by weight.

With regards to the chemical composition of each of the leucite, diopside and feldspar glass frits, together these preferably comprise one or more oxides of the following: silicon (e.g. SiO_2), aluminium (e.g. Al_2O_3), sodium (e.g. Na_2O), calcium (e.g. CaO), magnesium (e.g. MgO) and potassium (e.g. K_2O), which are typical glass-forming ingredients and which therefore contribute to attainment of the desirable properties of the composition hereinbefore described.

Advantageously, each of the leucite, diopside and feldspar glass frits may additionally further comprise one or more oxides of the following: aluminium (e.g. Al_2O_3), barium (e.g. BaO), boron (e.g. B_2O_3), cobalt (e.g. CoO, Co_2O_3, Co_3O_4), chromium (e.g. CrO, Cr_2O_3, CrO_2, CrO_3), indium (e.g. In_2O_3), nickel (e.g. NiO, Ni_2O_3), rubidium (e.g. Rb_2O) titanium (e.g. TiO_2) and zirconium (e.g. ZrO_2), and optionally also magnesium fluoride (MgF_2), to enable subtle changes in the colour of the final ceramic material to be achieved.

As discussed above, the ceramic material of the present invention possesses and exhibits a number of desirable properties, including preferably having a linear coefficient of thermal expansion (α) in the range of from 5 to 15 ppm/°C, further preferably in the range of from 7 to 12 ppm/°C, and most preferably in the range of from 9.5 to 10 ppm/°C, as measured using dilatometry over the temperature range 300-400 °C.

Advantageously therefore, the ceramic material of the invention may exhibit a percentage difference in linear coefficient of thermal expansion, as compared to a core

material to which it may be applied, of less than 10 %, preferably less than 5 % and most preferably of less than 1 % (when measured over the temperature range 300-400 °C). In real terms, such a percentage difference may equate to a difference of less than 1 ppm/°C and preferably of less than 0.5 ppm/°C (when measured over the temperature range 300-400 °C).

A ceramic material according to the invention may additionally possess a biaxial flexural strength of at least 80 MPa, preferably of at least 90 MPa, further preferably at least 100 MPa and possibly up to around 120 MPa. Biaxial flexural strength is measured as follows: prepare a fired disc of the ceramic material of the invention of 12 mm diameter and 2 mm thickness. Grind and polish this disc down to a thickness of 1.2 mm using silicon carbide grinding papers. A Lloyds LRX tensometer (available from Lloyds Instruments Ltd, UK) with a 2500 N load cell and a cross-head speed of 1 mm/min was used to determine the biaxial flexural strength. The disc was fractured using a ball on ring arrangement. After fracture, the disc was accurately measured with a digital calliper (available from Mitutoyo, Tokyo, Japan) to allow computation of the biaxial flexural strength using the equation:

$$\sigma_{max} = [P / h^2] \{(1 + v)[0.485 \times \ln(a / h) + 0.52] + 0.48\}$$

where σ_{max} is the maximum tensile strength, P the measured load at fracture in Newtons, h is the sample thickness in millilmetres, v is Poisson's ratio for the material (a value of 0.25 was substituted for the glass-ceramics) and a is the radius of the support ring in millimetres. In all cases, fracture was observed to have originated at the centre of the disc.

The greater the value of biaxial flexural strength exhibited, the more difficult it is for the material in question to fracture.

Furthermore, a ceramic material according to the invention may register a Vickers hardness (H_V) of at least 550 kg/mm^2, preferably of at least 555 kg/mm^2 and further preferably up to around 570 kg/mm^2. Vickers hardness is measured as follows: prepare a fired disc of the ceramic material of the invention of 12 mm diameter and 2 mm thickness. Grind and polish this disc down to a thickness of 1.2 mm using silicon carbide grinding papers and diamond paste. Make an indentation in the centre of a

surface of the disc using a VX Vickers Hardness Tester (available from Foundrax, Somerset, UK) with a load set at 9.8 N (1kg) and a pyramidal indenter until three acceptable crack patterns are obtained. Take readings of the diagonal length of the cracks using a Vanox™ optical microscope (available from Olympus Optical Co. Limited, Japan) equipped with a digital camera and a computer interface (KS400 software available from Imaging Associations Limit, Thames, UK). Calculate Vickers hardness using the following equation:

$$H_v = \frac{1.8544P}{d^2}$$

where P is the applied load in kilograms and d is the mean diagonal length in millimetres.

The greater the value of Vickers hardness exhibited, the more scratch and general wear resistance the material in question is likely to exhibit.

Beneficially, the ceramic material of the invention may exhibit an indentation fracture toughness (K_{Ic}) of at least 1.25 MPa·$m^{1/2}$, preferably of at least 1.3 MPa·$m^{1/2}$ and preferably up to around 1.55 MPa·$m^{1/2}$. Fracture toughness is measured as follows: prepare a 1.2 mm thick fired disc of the ceramic material of the invention and make an indentation in the same manner as for measuring Vickers hardness. Take readings of the radial crack length using the same equipment as used for measuring Vickers hardness and calculated the fracture toughness using the following equation:

$$K_{Ic} = \frac{xP}{c^{3/2}}$$

where x is a constant (0.0824), P is the applied load in Newtons and c is the radial crack length in metres.

The greater the value of fracture toughness exhibited, the more resistance the material in question has to crack propagation.

Moreover, the ceramic material of the invention preferably also exhibits resistance to thermal shock up to a temperature of at least 235 °C, preferably at least 250 °C and further preferably up to around 265 °C. This means that the material (when applied onto a chosen core material) can be heated to this temperature for 30 minutes before being quenched in ice water, dried, reheated to the same temperature and cooled to room temperature without showing signs of failure.

A second aspect of the invention provides a method of making a ceramic dental restoration material as hereinbefore described, said method comprising the steps of:

(a) preparing a diopside glass frit, a leucite glass frit and, optionally, a feldspar glass frit;

(b) grinding each glass frit of step (a) to produce glass frits powder(s) having an optimum particle size, preferably of less than 100 µm;

(c) blending a quantity of the powdered diopside glass frit with a quantity of the leucite glass frit and, optionally, a quantity of the feldspar glass frit to form a glass frit powder mixture; and

(d) further processing the glass frit powder mixture to form the restoration material of the invention.

The inventors have discovered that performance of such a method enables the making of a ceramic dental restoration material according to the first aspect of the invention, which exhibits one or more of the desirable properties hereinbefore described.

Grinding of each glass frit in step (b) may be achieved by milling, e.g. planetary ball milling, although any other suitable milling or particle size reduction technique may be used. The ground glass frits may then be sieved using appropriate sieving apparatus to achieve glass frit powders of optimum particle size.

The glass frit powders in step (c) may be blended in an appropriate ratio, especially as hereinbefore described, so as to enable production of a desired ceramic restoration material.

The further processing referred to in step (d) above may be any one of the following processes:

1) sintering, whereby the glass frit powder mixture may be made into a slurry by addition of water or other liquid (e.g. ethanol), applied to an appropriate metallic or high strength ceramic core, allowed to dry and subsequently fired at a sufficiently high temperature (e.g. in the range of from 900-1000 °C, especially 930 °C, for at least 5 minutes) in an appropriate firing oven (e.g. a Programat P300 IPS vacuum furnace available from Ivoclar Vivadent AG, Schaan, Liechtenstein) to ensure that the particles fuse together to form the desired crystalline phases;

2) hot-pressing, whereby the glass frit powder mixture may firstly be pelletized by filling pellet moulds (e.g. 11 mm diameter and 8 mm height) with the powder mixture, pressing the powder mixture in the mould to form pellets, removing the pellets from the mould and subsequently firing them at a sufficiently high temperature (e.g. in the range of from 900-1000 °C, especially 930 °C, for at least 5 minutes) in an appropriate firing oven (e.g. a Programat P300 IPS vacuum furnace available from Ivoclar Vivadent AG, Schaan, Liechtenstein) to ensure that the particles in the pellets fuse together to form the desired crystalline phases - the resultant fully crystallized solid pellets are then ready for use in hot-pressing;

3) CAD-CAM, whereby the glass frit powder mixture may firstly be formed into a block by filling, e.g. a stainless steel cuboid mould with the powder mixture, pressing the powder mixture in the cuboid mould to form a block, removing the block from the mould and subsequently firing it at a sufficiently high temperature (e.g. in the range of from 900-1000 °C, especially 930 °C, for at least 5 minutes) in an appropriate firing oven (e.g. a Programat P300 IPS vacuum furnace available from Ivoclar Vivadent AG, Schaan, Liechtenstein) to ensure that the particles in the block fuse together to form the desired crystalline phases - the resultant fully crystallized solid block is then ready for use in CAD-CAM.

A third aspect of the invention consequently provides a ceramic dental restoration precursor material for use in making a ceramic dental restoration material as hereinbefore described in the form of:

(i) a glass frit powder mixture blended in an appropriate ratio, especially as hereinbefore described, suitable for sintering;

(ii) fully crystallized solid pellets, formed from a combination of glass frits as hereinbefore described, suitable for hot-pressing; and/or

(iii) a fully crystallized solid block, formed from a combination of glass frits as hereinbefore described, suitable for use with CAD-CAM.

The composition of the diopside glass frit used in the invention preferably comprises the following ingredients:

SiO_2	50 to 70 % by weight
Al_2O_3	0 to 10 %
Na_2O	0 to 10 %
K_2O	0 to 5 %
MgO	5 to 20 %
CaO	10 to 25 %
ZrO_2	0 to 10 %
TiO_2	0 to 10 %
B_2O_3	0 to 5 %
MgF_2	0 to 5%

Preferably, all of the ingredients specified for inclusion in a glass frit used in the present invention are reagent grade raw materials.

Further preferably the composition of the diopside glass frit comprises the following ingredients:

SiO_2	55.7 % by weight
Al_2O_3	2 %
Na_2O	1.6 %
K_2O	2.4 %
MgO	11.8 %
CaO	16.5 %
ZrO_2	3 %
TiO_2	3 %
B_2O_3	2 %
MgF_2	2 %

The composition of the leucite glass frit used in the invention preferably comprises the following ingredients:

SiO_2	50 to 70 % by weight

Al_2O_3	10 to 20 %
Na_2O	0 to 20 %
K_2O	5 to 25%
MgO	0.5 to 5 %
CaO	0 to 10 %
BaO	0 to 10 %

Further preferably the composition of the leucite glass frit comprises the following ingredients:

SiO_2	58 % by weight
Al_2O_3	15 %
Na_2O	8 %
K_2O	13 %
MgO	1 %
CaO	2 %
BaO	3 %

The composition of the feldspar glass frit used in the invention preferably comprises the following ingredients:

SiO_2	60 to 80 % by weight
Al_2O_3	5 to 15 %
Na_2O	0 to 10 %
K_2O	0 to 10%
MgO	0.5 to 5 %
CaO	0 to 10 %
B_2O_3	0 to 10 %

with the proviso that the summed total of Na_2O, K_2O and CaO present in the composition is at least 5 %, and preferably at least 7 %, by weight.

Further preferably the composition of the feldspar glass frit comprises the following ingredients:

SiO_2	73 % by weight
Al_2O_3	8 %
Na_2O	5.5 %
K_2O	4 %

MgO	0.5 %
CaO	1.5 %
B_2O_3	7.5 %

As previously described herein, a ceramic dental restoration material according to the invention is suitable for (and especially designed for) use in dentistry, particularly aesthetic restorative dentistry, and especially as a veneering ceramic for dental crowns (both anterior and posterior), dental bridges, onlays and inlays.

When used for such purposes, the ceramic dental restoration material may be applied to either a metallic core material or a ceramic core material (especially to a high strength ceramic core material), or it may be resin-bonded directly to the enamel and/or dentine of an existing tooth. Because of the desirability of ceramic cores over metallic cores, it is especially preferred that the material be used in combination with a high strength ceramic core material. The primary benefit of such a combination lies in the optimised matching of linear coefficients of thermal expansion that can be achieved, thereby resulting in fewer (if any) failures of the final restoration.

Suitable metallic core materials for use with the ceramic material of the invention include: titanium, gold and precious metal alloys, and base metal alloys. Suitable ceramic core materials suitable for use with the ceramic material of the invention include: densely-sintered alumina (e.g. Procera™), zirconia-based materials, lithium disilicate (Li_2O-Al_2O_3-SiO_2) and fluorocanasite (Al_2O_3-CaO-F-K_2O-Na_2O-SiO_2) glass-ceramic core materials, and other of the materials listed in Table I.

For a better understanding, the present invention will now be more particularly described with reference to the following non-limiting examples, as accompanied by the following Figures, in which:

Figure 1 is a Differential Thermal Analysis (DTA) trace of a leucite glass ceramic material;

Figure 2 is a DTA trace of a diopside glass ceramic material;

Figure 3 is an X-Ray Diffraction (XRD) trace of the leucite glass ceramic of Figure 1; and

Figure 4 is an XRD trace of the diopside glass ceramic of Figure 2.

Example 1

A diopside glass was prepared (by melting the following reagent grade raw materials) having a composition (% by weight): SiO_2 55.7 %; Al_2O_3 2 %; Na_2O 1.6 %; K_2O 2.4 %; MgO 11.8 %; CaO 16.5 %; ZrO_2 3 %; TiO_2 3 %; B_2O_3 2 %; MgF_2 2 %. The molten glass was cooled quickly to make a diopside glass frit, which was then ground into a powder using planetary ball milling.

Similarly a leucite glass was prepared (by melting the following reagent grade raw materials) having a composition (% by weight): SiO_2 58 %; Al_2O_3 15 %; Na_2O 8 %; K_2O 13 %; MgO 1 %; CaO 2 %; BaO 3 %. The molten glass was cooled quickly to make a leucite glass frit, which was then ground into a powder using planetary ball milling.

Furthermore a feldspar glass was prepared (by melting the following reagent grade raw materials) having a composition (% by weight): SiO_2 73 %; Al_2O_3 8 %; Na_2O 5.5 %; K_2O 4 %; MgO 0.5 %; CaO 1.5 %; B_2O_3 7.5 %. The molten glass was cooled quickly to make a feldspar glass frit, which was then ground into a powder using planetary ball milling.

Each of these three glass frits was then blended to form two powder mixtures (having a maximum powder particle size of 100 μm) in the following ratios:

Powder Mixture 1 (PM1): leucite 58 %; diopside 22 %; feldspar 20 %

Powder Mixture 2 (PM2): leucite 60 %; diopside 20 %; feldspar 20 %.

Each of PM1 and PM2 were formed into glass ceramic rods (of 30 mm length and 6 m diameter) so as to enable determination of their linear coefficients of thermal expansion (α) using the following slip-moulding / slip-casting technique. A suspension (a “slip”) of each of PM1 and PM2 was made by dispersing each of the mixtures into water. Each slip was then poured into a rod-shaped, silicone rubber mould and water drawn out of the mould so as to compact the powder particles within. Once fully dried, the rods (of type R1 and R2 made from PM1 and PM2 respectively) were removed from their moulds and subsequently sintered (at 930 °C for 5 minutes).

Each rod was then smoothed and square cut at both ends by trimming and paralleling with a rotary diamond cutting machine (LECO VC-50 available from LECO Corporation,

Michigan, USA) with a diamond wafering blade (available from Buehler, Illinois, USA) and was fired following the recommended firing procedure.

Similarly, ceramic rods were produced from each of the following commercially available ceramics in the same manner as outlined above: VITA VM 9 (PM3) (available from Vita Zahnfabrik, Switzerland) forming rod type 3 (R3) and IPS e.max Ceram (PM4) (available from Ivoclar Vivadent AG, Liechtenstein) forming rod type 4 (R4).

Each of the rods were placed in an Electronic Dilatometer 402 EP (available from Netzsch, Germany) and the temperature was raised at a heating rate of 3 °C/min from 20 °C to 580 °C, followed by cooling to room temperature. Calibration of the dilatometer was performed by measurement of the linear coefficient of thermal expansion (α) of a standard quartz specimen. From the thermal expansion curves, α was calculated for all rods over the temperature range 300 °C to 400 °C using a computer software programme (EP programme SW/DIL/421.85) connected to the dilatometer; the means results (averaged three rods per type) are shown in Table II below:

Table II

	R1	R2	R3	R4
Mean Linear Coefficient of Thermal Expansion (α) ± Standard Deviation (ppm/°C)	9.7 ± 0.1	10.02 ± 0.02	8.7 ± 0.2	9.3 ± 0.1

To test the compatibility of each of the sample ceramic materials (R1-R4) with core materials, ceramic rods were also fabricated from both fluorocanasite (i.e. Al_2O_3-CaO-F-K_2O-Na_2O-SiO_2) (R5) VITA In-Ceram YZ (R6), a partially yttrium-stabilized zirconium dioxide high strength ceramic core material (also available from Vita Zahnfabrik, Switzerland).

From the thermal expansion curves, α was again calculated for all R5 and R6 rods over the temperature range 300 °C to 400 °C in the same manner as described above; the means results (averaged three rods per type) are shown in Table III below:

Table III

	R5	R6
Mean Linear Coefficient of Thermal Expansion (α) ± Standard Deviation (ppm/°C)	9.7 ± 0.07	10.5 ± 0.1

As is clearly shown, glass ceramic R1 has a mean linear coefficient of thermal expansion that substantially matches that of core material R5 (unlike prior art glass ceramics R3 and R4 which have lower coefficients). Similarly, glass ceramic R2 has a mean linear coefficient of thermal expansion that substantially matches that of core material R6 (again unlike prior art glass ceramics R3 and R4 which have lower coefficients). Such positive matching between each of R1 and R5, and R2 and R6, enables production of two alternative all-ceramic restorations having the desired mechanical properties (discussed above).

Example 2

Multiples of ten discs (of 12 mm diameter and 1 mm thickness) were fabricated from each of the core materials fluorocanasite (D1) and VITA In-Ceram YZ (D2) used in Example 1. Each batch of ten D1 discs was provided with a 0.7 mm thick veneering layer of one of each of the PM1, PM3 and PM4 glass ceramics used in Example 1, whilst each batch of ten D2 was provided with a 0.7 mm thick veneering layer of one of each of the PM2, PM3 and PM4 glass ceramics used in Example 1.

Each veneered disc was subsequently preheated to 90 °C for 30 minutes, quenched in ice cold water, dried, reheated to 90 °C and finally cooled back to room temperature. Each veneered disc was then inspected for crazing using optical microscopy (Wild M3Z microscope available from Wild Heerbrugg, Switzerland) at 40x magnification with fibre optic transillumination (Intralux 4000, Switzerland). The results are as follows.

None of the veneered discs exhibited crazing or cracking (which would constitute failure) during the 0-90 °C temperature cycle (ΔT = 90 °C). As such, each veneered disc was subjected to further heat/cool testing (as above), successively increasing the temperature by 10 °C increments, until failure. The results of are shown in Table IV below.

Table IV

	D1			D2		
	PM1	**PM3**	**PM4**	**PM2**	**PM3**	**PM4**
Mean ΔT ± Standard Deviation (°C)	239 ± 25.1	170 ± 23	198 ± 16	250 ± 12.5	179 ± 18	192 ± 12
ΔT Range (°C)	200 - 270	160 - 200	170 - 210	230 - 270	150 - 200	170 - 210

Clearly, the combinations of PM1 and PM2 with each of D1 and D2 respectively exhibits the highest mean ΔT results, meaning that these combinations can withstand the largest range of temperature cycle before failing. These characteristics are a direct consequent of the significantly higher thermal compatibility of Sample PM1 with D1, and of PM2 with D2, as compared to the commercial glass ceramics PM3 and PM4 with either of D1 or D2.

Example 3

A leucite glass was prepared (by melting the following reagent grade raw materials) having a composition (% by weight): SiO_2 58 %; Al_2O_3 15 %; Na_2O 8 %; K_2O 13 %; MgO 1 %; CaO 2 %; BaO 3 %. The molten glass was cooled quickly to make a leucite glass frit, which was then ground into a powder using planetary ball milling. This powder was used to produce discs (of 12 mm diameter and 2 mm thickness) which were then heat treated in an air furnace at 830 °C for 30 minutes in order to produce leucite glass ceramic discs.

Similarly a diopside glass was prepared (by melting the reagent grade raw materials) having a composition (% by weight): SiO_2 55.7 %; Al_2O_3 2 %; Na_2O 1.6 %; K_2O 2.4 %; MgO 11.8 %; CaO 16.5 %; ZrO_2 3 %; TiO_2 3 %; B_2O_3 2 %; MgF_2 2 %. The molten glass was cooled quickly to make a glass frit, which was then ground into a powder using planetary ball milling. This powder was again used to produce discs (of 12 mm diameter and 2 mm thickness) which were then heat treated in an air furnace at 930 °C for 60 minutes in order to produce the diopside glass ceramic discs.

Prior to production of discs, each powder was characterised using DTA – the results are shown in Figures 1 and 2. As can be seen in these Figures, the leucite glass ceramic exhibited a glass transition temperature (T_g) of 653 °C and a crystallisation

temperature (T_x) of 780 °C. Similarly, the diopside glass ceramic exhibited a exhibited a glass transition temperature (T_g) of 720 °C and crystallisation temperatures (T_x) of 847 °C and 917 °C. Post heat-treatment, the discs were ground down to powders once more and characterised using XRD – the results are shown in Figures 3 and 4.

In the next step, the two glass-ceramics were blended, and for this, two alternative methods were performed. One method involved blending of the fully crystallized (i.e. fired) form of the leucite glass ceramic pellets with the fully crystallized (i.e. fired) form of the diopside glass ceramic pellets to form Blend A, whilst the other method involved blending of the non-fired leucite glass ceramic pellets with the non-fired diopside glass ceramic pellets to form Blend B.

To make Blend A, three different mixtures of fully crystallized pellets were used:

(1) Blend A1: 90 % leucite pellets and 10 % diopside pellets
(2) Blend A2: 80 % leucite pellets and 20 % diopside pellets
(3) Blend A3: 70 % leucite pellets and 30 % diopside pellets.

Similarly, to make Blend B, three different mixtures of non-fired pellets were used:

(1) Blend B1: 70 % leucite pellets and 30 % diopside pellets
(2) Blend B2: 60 % leucite pellets and 40 % diopside pellets
(3) Blend B3: 50 % leucite pellets and 50 % diopside pellets.

Each of Blends A1, A2, A3 and B1, B2, B3 were subsequently heated in a vacuum furnace at 930 °C and characterized using XRD and optical microscopy. Figures 5 and 6 show XRD traces for each of Blends A1 (upper trace), A2 (centre trace), A3 (lower trace) and B1 (upper trace), B2 (centre trace), B3 (lower trace) respectively; all showing the presence of both leucite crystallites and diopside crystallites. However, optical microscopy of the two blends shows Blends A1, A2, A3 (in Figure 5) as having crystal grains but undesirable porosity within the material, making it (and therefore its method of making) less attractive as compared to Blends B1, B2, B3 (in Figure 6) which again show crystal grains, but pleasingly no porosity.

Example 4

Glass ceramic discs of Powder Mixture 2 (PM2) and Powder Mixture 3 (PM3) from Example 1 were compared to determine the relative performance of each ceramic material in terms of mechanical properties; these results are shown in Table V overleaf.

Table V

Property	PM2	PM3
Crystalline Phase(s) (SEM and XRD)	Leucite & Diopside	Leucite
Linear Coefficient of Thermal Expansion (α) (ppm/°C) (at 300-400 °C)	10.0	8.8
Biaxial Flexural Strength (MPa)	109 ± 8	79 ± 11
Vickers Hardness (kg/mm^2)	561 ± 9	527 ± 17
Fracture Toughness ($MPa \cdot m^{1/2}$)	1.4 ± 0.13	1.16 ± 0.04
Chemical Solubility ($\mu g/cm^2$)	6	6
Thermal Shock Resistance (°C)	250 ± 13	179 ± 18

As is clearly shown, the ceramic formed from PM2 outperforms the ceramic formed from PM3 in all aspects (apart from chemical solubility where the two are equally matched), illustrating the benefit of such a multi-phase structure as compared to prior art two-phase structures, with the attendant performance and longevity benefits described above.

CLAIMS:

1. A ceramic dental restoration material having a composition comprising a diopside crystalline phase and a leucite crystalline phase.

2. A ceramic material as claimed in claim 1 formed from the following combinations of glass frits:

   20 to 60 % by weight (preferably 30 to 50 %) of a diopside glass frit

   40 to 80 % by weight (preferably 50 to 70 %) of a leucite glass frit.

3. A ceramic material as claimed in claim 1 wherein both the diopside crystalline phase and the leucite crystalline phase are dispersed in a feldspathic glassy matrix.

4. A ceramic material as claimed in claim 3 formed from the following combinations of glass frits:

   10 to 40 % by weight (preferably 10 to 22 %) of a diopside glass frit

   50 to 80 % by weight (preferably 58 to 70 %) of a leucite glass frit

   5 to 25 % by weight (preferably 10 to 20 %) of a feldspar glass frit

   with the proviso that the sum total amount of the glass frits is at least 80-100 %, with the remaining 0-20 % being one or more other ingredients included in the composition.

5. A ceramic material as claimed in claim 4 wherein the sum total amount of the glass frits is 100 %.

6. A ceramic material as claimed in claim 4 wherein the composition further comprises one or more oxides of the following: titanium, cerium, tin and vanadium in a total amount of from 0 to 20 % by weight, preferably from 0.0001 to 10 % by weight and more preferably from 0.0005 to 5% by weight.

7. A ceramic material as claimed in any preceding claim wherein each of the leucite, diopside and feldspathic phases (where present) comprises one or more oxides of the following: silicon, aluminium, sodium, calcium, magnesium and potassium.

8. A ceramic material as claimed in any claim 7 wherein each of the leucite, diopside and feldspathic phases (where present) further comprise one or more oxides of the following: aluminium, barium, boron, cobalt, chromium, indium, nickel, rubidium, titanium, zirconium, and optionally also magnesium fluoride.

9. A ceramic material as claimed in any preceding claim having a linear coefficient of thermal expansion (α) in the range of from 5 to 15 ppm/°C, as measured using dilatometry over the temperature range 300-400 °C.

10. A ceramic material as claimed in claim 9 having α in the range of from 7 to 12 ppm/°C, as measured using dilatometry over the temperature range 300-400 °C.

11. A ceramic material as claimed in claim 10 having α in the range of from 9.5 to 10 ppm/°C, as measured using dilatometry over the temperature range 300-400 °C.

12. A ceramic material as claimed in any of claims 9, 10 or 11 having a percentage difference in linear coefficient of thermal expansion, as compared to a core material to which it may be applied, of less than 10 %, preferably of less than 5 % and most preferably of less than 1 %, when measured over the temperature range 300-400 °C.

13. A ceramic material as claimed in any preceding claim having a biaxial flexural strength of at least 80 MPa.

14. A ceramic material as claimed in claim 13 having a biaxial flexural strength of at least 90 MPa and preferably up to around 120 MPa.

15. A ceramic material as claimed in any preceding claim having a Vickers hardness of at least 550 kg/mm^2.

16. A ceramic material as claimed in claim 15 having a Vickers hardness of at least 555 kg/mm^2 and preferably up to around 570 kg/mm^2.

17. A ceramic material as claimed in any preceding claim having an indentation fracture toughness of at least 1.25 MPa·$m^{1/2}$.

18. A ceramic material as claimed in claim 17 having an indentation fracture toughness of at least 1.3 MPa·$m^{1/2}$ and preferably up to around 1.55 MPa·$m^{1/2}$.

19. A ceramic material as claimed in any preceding claim which exhibits resistance to thermal shock up to a temperature of at least 235 °C.

20. A ceramic material as claimed in claim 19 which exhibits resistance to thermal shock up to a temperature of at least 250 °C and preferably up to around 265 °C.

21. A method of making a ceramic dental restoration material as claimed in claim 1 comprising the steps of:

(a) preparing a diopside glass frit, a leucite glass frit and, optionally, a feldspar glass frit;

(b) grinding each glass frit of step (a) to produce glass frits powders having an optimum particle size, preferably of less than 100 µm;

(c) blending a quantity of the powdered diopside glass frit with a quantity of the leucite glass frit, and optionally, a quantity of the feldspar glass frit to form a glass frit powder mixture; and

(d) further processing the glass frit powder mixture to form the restoration material of the invention.

22. A method according to claim 21 wherein grinding of each glass frit in step (b) is achieved by milling, e.g. planetary ball milling, or any other suitable milling or particle size reduction technique.

23. A method according to claim 22 wherein the ground glass frits are sieved using appropriate sieving apparatus to achieve glass frit powders of optimum particle size.

24. A method according to any of claims 21 to 23 wherein the further processing of step (d) is any one of the following processes:

1) sintering of a slurry of the glass frit powder mixture;
2) hot-pressing of fired pellets of the glass frit powder mixture;
3) CAD-CAM using a fired block of material made from the glass frit powder mixture.

25. A method according to any of claims 21 to 23 wherein the composition of the diopside glass frit comprises the following ingredients:

SiO_2	50 to 70 % by weight
Al_2O_3	0 to 10 %
Na_2O	0 to 10 %
K_2O	0 to 5 %
MgO	5 to 20 %
CaO	10 to 25 %
ZrO_2	0 to 10 %
TiO_2	0 to 10 %
B_2O_3	0 to 5 %
MgF_2	0 to 5%

26. A method according to claim 21 wherein the composition of the diopside glass frit comprises the following ingredients:

SiO_2	55.7 % by weight
Al_2O_3	2 %
Na_2O	1.6 %
K_2O	2.4 %
MgO	11.8 %
CaO	16.5 %
ZrO_2	3 %
TiO_2	3 %
B_2O_3	2 %
MgF_2	2 %

27. A method according to any of claims 21 to 26 wherein the composition of the leucite glass frit comprises the following ingredients:

SiO_2	50 to 70 % by weight
Al_2O_3	10 to 20 %

Na_2O	0 to 20 %
K_2O	5 to 25%
MgO	0.5 to 5 %
CaO	0 to 10 %
BaO	0 to 10 %

28. A method according to 27 wherein the composition of the leucite glass frit comprises the following ingredients:

SiO_2	58 % by weight
Al_2O_3	15 %
Na_2O	8 %
K_2O	13 %
MgO	1 %
CaO	2 %
BaO	3 %

29. A method according to any of claims 21 to 28 wherein the composition of the feldspar glass frit comprises the following ingredients:

SiO_2	60 to 80 % by weight
Al_2O_3	5 to 15 %
Na_2O	0 to 10 %
K_2O	0 to 10%
MgO	0.5 to 5 %
CaO	0 to 10 %
B_2O_3	0 to 10 %

with the proviso that the summed total of Na_2O, K_2O and CaO present in the composition is at least 5 %, and preferably at least 7 %, by weight.

30. A method according to claim 29 wherein the composition of the feldspar glass frit comprises the following ingredients:

SiO_2	73 % by weight
Al_2O_3	8 %
Na_2O	5.5 %
K_2O	4 %
MgO	0.5 %

CaO	1.5 %
B_2O_3	7.5 %

31. A ceramic dental restoration precursor material for use in making a ceramic dental restoration material as claimed in claim 1 in the form of:
    (i) a glass frit powder mixture blended in an appropriate ratio suitable for sintering;
    (ii) fully crystallized solid pellets, formed from a combination of glass frits, suitable for hot-pressing; and/or
    (iii) a fully crystallized solid block, formed from a combination of glass frits, suitable for use with CAD-CAM.

32. Use of a ceramic dental restoration material as claimed in claim 1 as a veneering ceramic for dental crowns, dental bridges, onlays and inlays.

33. Use of a ceramic dental restoration material as claimed in claim 32 with either a metallic core material or a ceramic core material.

34. Use of a ceramic dental restoration material as claimed in claim 33 wherein the metallic core material is titanium, gold or a precious metal alloy, or a base metal alloy.

35. Use of a ceramic dental restoration material as claimed in claim 33 wherein the ceramic core material is a high strength ceramic material chosen from a zirconia-based material or a fluorocanasite glass-ceramic core material.

36. Use of a ceramic dental restoration material as claimed in claim 32 for resin-bonding directly to the enamel and/or dentine of an existing tooth.