	TANDARD PATENT(11) Application No. AU 2003238041 B2USTRALIAN PATENT OFFICE							
(54)	Title Opalescent glass-ceramic product							
(51)	International Patent Classification(s) A61K 6/06 (2006.01) C03C 4/00 (2006.01) A61K 6/027 (2006.01) C03C 10/00 (2006.01) C03C 3/097 (2006.01) C03C 10/10 (2006.01)							
(21)	Application No: 2003238041 (22) Date of Filing: 2003.06.24							
(87)	WIPO No: WO04/000743							
(30)	Priority Data							
(31)	Number(32)Date(33)Country102 28 381.82002.06.25DE							
(43) (43) (44)	Publication Date:2004.01.06Publication Journal Date:2004.03.04Accepted Journal Date:2008.07.03							
(71)	Applicant(s) Degudent GmbH							
(72)	Inventor(s) Krumbholz, Klaus							
(74)	Agent / Attorney Patent Attorney Services, 26 Ellingworth Parade, Box Hill, VIC, 3128							
(56)	Related Art US 6280863 EP 0885855 EP 0622342							

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum Internationales Büro



- (43) Internationales Veröffentlichungsdatum 31. Dezember 2003 (31.12.2003)
- (51) Internationale Patentklassifikation⁷: C03C 3/097, 4/00, A61K 6/06
- (21) Internationales Aktenzeichen: PCT/EP2003/006644
- (22) Internationales Anmeldedatum: 24. Juni 2003 (24.06.2003)
- (25) Einreichungssprache: Deutsch
- (26) Veröffentlichungssprache: Deutsch
- (30) Angaben zur Priorität: 102 28 381.8 25. Juni 2002 (25.06.2002) DE
- (71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): DEGUDENT GMBH [DE/DE]; Rodenbacher Chaussee 4, 63457 Hanau (DE).

(72) Erfinder; und

- (75) Erfinder/Anmelder (nur f
 ür US): KRUMBHOLZ, Klaus [DE/DE]; Gr
 ünewaldstr. 3, 63225 Langen (DE).
- (74) Anwalt: STOFFREGEN, Hans-Herbert; Friedrich-Ebert-Anlage 11b, 63450 Hanau (DE).

(10) Internationale Veröffentlichungsnummer WO 2004/000743 A1

(81) Bestimmungsstaaten (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CII, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS. JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Bestimmungsstaaten (regional): ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

- mit internationalem Recherchenbericht
- vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: OPALESCENT GLASS-CERAMIC PRODUCT

(54) Bezeichnung: OPALESZIERENDE GLASKERAMIK

(57) Abstract: The invention relates to an opalescent glass-ceramic product, especially an opalescent glass-ceramic product as a dental material or as an additive to or component of dental material, comprising at least the components SiO_2 , Al_2O_3 , P_2O_5 , Na_2O_5 , K_2O_5 , CaO and $Me(IV)O_2$. In order to obtain improved opalescence with improved transparency, in addition to fluorescence, thermal expansion and a combustion temperature adapted to other materials, the opalescent ceramic product is devoid of ZrO_2 and TiO_2 , such that the Me(II)O content in the glass ceramic is less than approximately 4 wt. % and the $Me(IV)O_2$ content amounts to approximately 0.5 - 3 wt. %. The invention also relates to a method for the production of the opalescent glass-ceramic product. The glass-ceramic product can be used as dental material or as an additive to or a component of dental material.

(57) Zusammenfassung: Opaleszierende GlaskeramikDie Erfindung bezieht sich auf eine opaleszierende Glaskeramik, insbesondere eine opaleszierende Glaskeramik als Dentalmaterial oder als Zusatz zu oder Bestandteil von Dentalmaterial, umfassend zumindest die Komponenten SiO₂, Al₂O₃, P₂O₅, Na₂O, K₂O, CaO sowie Me(IV)O₂. Um eine verbesserte Opaleszenz bei gleichzeitig verbesserter Transparenz sowie eine auf andere Materialien abgestimmte Brenntemperatur und Wärmedehnung sowie Fluoreszenz zu erreichen ist vorgesehen, dass die opaleszierende Keramik ZrO₂ und TiO₂ frei oder im Wesentlichen von ZrO₂ und TiO₂ frei ist, dass die Glaskeramik einen Me(II)O-Gehalt von weniger als in etwa 4 Gew.-% aufweist und dass der Me(IV)O₂ - Gehalt in etwa 0,5 bis 3 Gew.-% beträgt. Ferner wird ein Verfahren zur Herstellung der opaleszierenden Glaskeramik vorgeschlagen. Die Glaskeramik kann als Dentalmaterial oder als Zusatz zu oder Bestandteil von Dentalmaterial verwendet werden.

Description

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Opalescent Glass Ceramic

5 The invention relates to an opalescent glass ceramic, in particular an opalescent glass ceramic as a dental material or as an additive to or component of dental material, comprising at least the components SiO₂, Al₂O₃, P₂O₅, Na₂O, K₂O, CaO and Me(IV)O₂. Furthermore, the invention relates to a method for producing an opalescent glass ceramic as well as to the use of such a ceramic.

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Opalescent glasses are known, for example, from EP 0 622 342 B1. EP 0 622 342 B1 discloses an opalescent glass based on $SiO_2 - B_2O_3 - Al_2O_3 - K_2O - Na_2O - CaO - BaO - SrO - TiO_2 - ZrO_2 - P_2O_5 - CeO_2$. The linear thermal expansion coefficients (TEC) therein are either much too high (Examples 5, 15, 26, 27 with TEC \ge 15.1) or much too low (TEC \le 10.8) to be usable for the preferred use of the material as a veneer ceramic for metal tooth restoration in pure form. To coat current alloys, a blending with further glasses is required.

Moreover, tests have shown that the glass ceramic products known from EP 0 622 342 B1 are too dull, so that a good aesthetic appearance is not ensured. Overall, the opalescent glass ceramic products known from EP 0 622 342 B1 exhibit a too weak and only slightly bake-stable opalescence, and a too high opacity and have no fluorescence.

A porcelain material intended for the dental field is known from US 6,022,819. It has TiO_2 or ZrO_2 as components. The SiO₂ content is preferably 50 to 85% by weight.

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The object of the present invention is to make available an opalescent glass ceramic product, a method for producing same as well as its use, which has improved opalescence with simultaneously improved transparency and a baking temperature or thermal expansion coefficients adapted to other materials as well as fluorescence.

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According to the invention, the object is essentially achieved by an opalescent glass ceramic product of the aforementioned type in which the opalescent glass ceramic is devoid of ZrO_2 and TiO₂, the glass ceramic product has a Me(II)O content of less than 4% by weight and the Me(IV)O₂% by weight is from 0.5 to about 3% by weight. Preferably, it is provided that the Me(IV)O₂ content is composed of 0 - 1% by weight CeO₂ and O - 2.5% by weight SnO₂.

In particular, the Me(II)O content is 2 - 3.5% by weight, preferably 2.5 - 3% by weight.

A preferred composition contains the following components:

Component	% by weight
SiO ₂	55 - 62
Al ₂ O ₃	13 - 17
B ₂ O ₃	0 - 2
P ₂ O ₅	1.5 - 3
Li ₂ O	0 - 2
Na ₂ O	7 - 12
K ₂ O	8 - 12
MgO	0 - 2
CaO	1 - 4
BaO	0 - 2
Tb ₂ O ₃	0 - 3
Me(IV)O ₂	0.5 - 3

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the indicated amount of Me(IV)O₂ being composed of 0 - 1% by weight of CeO₂ and 0 - 2.5% by weight SnO₂.

In particular, the composition of the glass ceramic is distinguished by:

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% by weight Component SiO₂ 58 - 60 14 - 15 Al_2O_3 P_2O_3 2.3 - 2.6 Na₂O 9.5 - 10.5 K₂O 9 - 10 CaO 2.8 - 3.0 SnO_2 1.3 - 1.6 0.3 - 0.4 CeO, 0 - 2.0 Tb₂O₃

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According to the invention, an improved opalescence is obtained by demixing of the glasses based on P_2O_5 and SnO_2 contents. The thermal expansion coefficient (TEC) of the ceramic according to the invention is in the range of 9.0 - 13.5 x 10⁻⁶/K and can be controlled by the K₂O

content.

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By additionally fusing CeO_2 and/or Tb_2O_3 , it can be attained that the glass ceramic fluoresces, a desirable property for dental ceramics. A strong, neutral fluorescence is obtained by combining both oxides.

Furthermore, the applicable baking temperature of the ceramic can be controlled by the portion of B_2O_3 , Li_2O and Na_2O and adapted to desired values. The applicable relevant baking temperature of the ceramics according to the invention are in the range of 870 to 970°C.

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On the whole, a glass ceramic is provided which satisfies all requirements with regard to aesthetic coating ceramics.

A method for producing the glass ceramic according to the invention is characterized by the following procedural steps:

- 1) weighing in the components according to one of the claims 1 to 6;
- 2) preferably mixing the mixture in a gyro mixer;
- melting the mixture in a preferably gas-heated furnace such as a drip-feed crucible furnace, preferably at about 1500°C;
- quenching the molten mass coming out of the furnace in a water bath and subsequent drying;
- 5) short grinding of the frit thus obtained in a mill (e.g. ball mill);
- 6) tempering the frit;
- 25 7) after drying, filling the frit in a mill, such as a ball mill, and grinding, preferably to about 10000 revolutions;
 - 8) sifting the ground frit through a sieve, the sieve opening forming the end.

Preferably, the frit is tempered in the following manner:

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- a. stacking the ground frits on quartz-coated fire-clay plates,
- b. placing the fire-clay plates in a furnace (e.g. electric furnace) heated to about 960°C,
- c. removing the plates from the furnace after about 40 minutes,
- d. quenching the fused frit cakes in a water bath.

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The ground frit is preferably sifted through a sieve having a mesh size M in the range of 80 μ m \leq M \leq 120 μ m, preferably M = 100 μ m.

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Unlike the glass ceramic known from EP 0 622 342 B1, the glass ceramic according to the invention needs no ZrO_2 and TiO_2 and the Me (II)O content remains less than 3% by weight. Moreover, by melting in CeO₂ and Tb₂O₃, the opal ceramic of the invention exhibits fluorescence. Furthermore, the baking temperature can be adapted to the desired application. The thermal expansion can be set by selective leucite crystallization in the ceramic according to the invention in such a way that it can be used especially for coating metal frame materials.

Further details, advantages and features of the invention can be found not only in the claims, the features found in them, alone and/or in combination, but also in the preferred embodiments found in the following description.

The invention will be described with reference to the following embodiments, wherein the Tests 1, 2, 8 to 21 are preferred and Tests 11 and 13 especially preferred. The compositions of the opal ceramic can be found in Table 1.

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Test	lvo.15	1	2	3	4.	5	6	7	8	9	10	11	12
% by weig	çlıt												
SiO2	55.34	59.78	\$9.05	60.01	58.03	56.22	59.83	55.53	58.44	58.93	58.02	59.08	58.72
A1203	16.09	14.52	14.63	16.45	15.91	16.83	16,4	14.71	14.23	34.44	14.34	14.48	14.78
B2O3	0.22	0.44	0.44			1.09	1.07	2.23	0.44		1.1		
P205	2.59	2.32	2.42	2.33	2.38	2.06	1,4	2.46	2.44	2.43	2.43	2.43	2.44
Li20	1		[1.28	1.31	1.1	1.29	0.45					
Na2O	9.08	9.36	9.3	4.44	6.39	5.91	6	9.97	9.84	10.03	10.01	10.04	9.13
K20	11.88	9.09	9.23	13.49	12.96	13.11	12.86	10	9.63	9.21	9.15	9.24	10.19
MgO													
CaO	2.6	2.97	2.95	0.09	1.3	1.91	0.09	2.88	2.98	2.97	2.97	2.97	2.97
BaO	11											1	
Tb2O3													
SnO2		1.52	0.88	0.85	0.86	0.87		1.45	0.89	0.88	0.88	1.43	1.44
CeO2	11		1.1	1.06	0.86	0.87	1.07	0.33	1.11	1.1	1.1	0.33	0.33
Z102	E.9												
TiO2	0.3												
Caiculat	ed thennal exp	ansion coeffi	cient (Alpha)	ct0exp6/K)									
	10.73	9.91	9.98	9.64	10.53	10.23	9. 9 6	10.58	10.35	10.31	10.02	10.32	10.28
Applicable	relevant bakin	g temperature	e in *C										·
	960	940	940	980	920	940	940	870	920	940	920	940	950
Tempering	of the glass firi	t (Min./ºC)									<u></u>		
[60/950	30/950	30/950		30/950		30/950	30/980	30/930	30/960	30/940		40/960
Measured th	bennal expansi	ion coefficier	1						·•				<u> </u>
	unkitown	unknown	9.71		แปลเองท		17	unknown	12.01	unknown	unknown.	11.08	ī 2.8
Optical value	ues												
L*trans.	69.7	77 1	76.6		Dull	*·	81.4	65.8	79.8	80.5	80.9	81	79
b*trans. b*ref.	26.5	31.6	32.8				9.4	27.4	25.6	29.3	34,9	30.3	32.9

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TABLE I (Columns 1 - 12)

Test	13	13 2r/Fi	14	15	16	17	18	19	20	21	22
by weight									-l		
SiO2	58.48	58.48	\$7.19	58.97	58.l	57.19	57.67	\$7.86	57.86	58.22	58.22
AI2O3	i4 61	l4.6l	14.31	14.66	14.51	i4.31	14.41	14.43	14.43	i4.62	1 14.7
B2O3				1							•
P2O5	2.44	2 44	2.44	2.04	2.85	2.44	2.44	2.44	2,44	2.46	2.5 j
Li2O	· · · · · · · · · · · · · · · · · · ·							<u> </u>			0.67
Na2O	9.9	9.9	9.85	9.91	9.88	9.85	9.80	9.87	9.87	9.19	9.21
K2O	9.93	9.93	9.79	9.8	10.03	9.79	9.82	9.86	9.86	10.94	10.1
MgO			<u> </u>			1	+ 			ļ	1.43
CaO	2.86	2.86	2.67	2.86	2.85	2.67	2.67	2.67	2.67	2.83	0.07
BaO											1.3
Tu2O3		÷	1.99			1.99	L.99	1.99	1.99		
SHO2	44		1.44	3.44	1.44	1.77	0.88	0.44		1.42	L 15
CeO2	0.33		0.33	0.33	0.33		U.22	0.44	0.88	0.33	0.33
2102		1 22					···				
TiO2		0.55					··················				
Calculated Th	ennal Expansi	u coefficient (Alph	a x10exp6)		k	I	i	I	1		
	10.49	10.45	10.52	10.41	10.56	10.52	10.54	10.54	10.54	10.55	10.44
pplicable relev	vant baking ter	nperature in °C	4		4	I	L	L		4	
	950	950	960	950	950	950	950	950	950	950	930
The second second	the glass frit *	(Idan PC)		· · · · · · · · · · · · · · · · · · ·	• • • · · · · · · · · · · · · · · · · ·			·			
Tenij)ersng or	40 /960	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/940
Aasured them	al expansion (Coefficien	L		l				44756	40/900	40/940
icanaeu (netti	12.6	10.59	11.5	11.24	L1.U8	10.53	unknown	Laiknowa	12.34	13.23	utiknow
ptical values		<u>)</u>	1	L	<u> </u>	<u></u>	<u> </u>	L	l	l	1
	80	78.9	80.3	83.3	78.1	82.6	79.5	80.2	75.2	76	71.3
L*trans	1 40			I						1	1

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TABLE I (Columns 13 - 22)

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A comparison of the tests shows that the thermal expansion coefficient of the glass ceramic according to the invention is controllable. Thus, a thermal expansion coefficient (TEC) in the range of 9.0 to 13.5 x 10^{-6} can be set. In comparison to the ceramics known from EP 0 622 342 B1, which have either too low a TEC ($\leq 11 \times 10^{-6}/K$) or a too high TEC ($\geq 16 \times 10^{-6}/K$), the glass ceramic according to the invention can be set in the TEC range of 11.0 to 13.0 x $10^{-6}/K$ for coating ceramics, which is especially important in the dental field.

Tests have shown that the SnO_2 - and/or CeO_2 - content is suitable for stimulating the crystallization of small amounts of leucite which are required for increasing the TEC.

A comparison of Test 13 with 1.44% SnO₂ with a Test in which the SnO₂ was replaced by ZrO₂ and TiO₂ according to the claims of EP 0 622 342 B1 (Test "13 Zr/Ti" in the Table), clearly shows that, in the latter Test, the TEC corresponds approximately to the mathematically determined value, assuming a homogeneous glass, which can indicate the lack of a leucite crystallization.

The examples show that the TEC in the glass ceramic of the invention can be controlled by the K_2O content when there is a sufficient Al_2O_3 content. In particular, Tests 11 to 14 and 21 show this property. Tests 15 and 16 indicate that the P_2O_5 content, which determines the extent of the phase separation of the glass, also has an effect.

By additionally fusing in CeO_2 and/or Tb_2O_3 , the glass ceramic can be caused to fluoresce. It could thereby be ascertained that fusing in only CeO_2 results in weak bluish fluorescence and Tb_2O_2 in a stronger yellow fluorescence which is not typical for natural teeth. A strong, neutral fluorescence is only obtained with a combination of both oxides, as Tests 17 to 20 show. The Tests 19 and 20 are optimal for fluorescence.

The baking temperature of the glass ceramic can be controlled by the proportion of B_2O_3 , Li_2O_3 and Na_2O and adapted to the desired value, as Tests 10 and 12 show. The applicable relevant baking temperatures of the glass ceramics according to the invention are in the range of 870°C to 970°C.

Test 13 has all of the preferred properties. The baking temperature and the TEC are ideal and, at the same time, the optical values with a transparency of L* (Transparency) = 80 and a Δb^* = 32.9 are very good. In comparison thereto, the ceramic (Ivo. 15) prepared according to EP 0 622 342 B1 only has a Δb^* of 26.5 at a transparency of L* (transp.) = 69.7.

It should be noted that the chemical stability and bending strength of the illustrated examples meet the requirements of the relevant standards for dental ceramics (ISO 9693).

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The exemplary embodiments according to Tests 13, 15 and 16 show the effect of the P_2O_5 content. Example 13 with a P_2O_3 content of 2.44% by weight is considered optimal, while the transparency is increased at the expense of opalescence in Example 15 with a P_2O_5 content of 2.04% by weight and an increased opalescence with reduced transparency can be ascertained in

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Example 16 with a P_2O_5 content of 2.85% by weight.

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Table 1 also shows embodiments (Tests 3, 4, 5, 6, 7 and 22) whose compositions are outside of the claimed range. In this case, Tests 3 to 5 have a too high K_2O content and additionally Test 3 has too little CaO. It has been found shown that these exemplary embodiments are already too dull in the untempered state, presumably due to a too strong leucite crystallization. In spite of a too high leucite content, Test 6 is transparent since it only has a slight tendency to demix due to a P_2O_5 content of less than 1.5% by weight, but its opalescence is too low. In Test 7, a too high B_2O_3 content results in a strong dullness and, in Test 22, CaO was replaced by MgO nd BaO which resulted in a reduced opalescence.

The glass ceramics according to the invention were produced according to the following method:

- 1. Weighing in the raw materials as noted in Table 1.
- 15 2. Mixing the mixture in a gyro mixer.
 - 3. Melting the mixture in a gas-heated drip-feed crucible furnace at about 1500°C.
 - 4. Quenching the molten mass running out of the furnace in a water bath.
 - 5. Drying the molten mass.
 - 6. Brief grinding of the frit thus obtained in a ball mill.
 - 7. Tempering the frit in the following manner:
 - stacking the ground frits on quartz-coated fire-clay plates
 - placing these plates in an electric furnace heated to 960°C
 - removing the plates from the furnace after about 40 minutes
 - quenching the fused frit cakes in the water bath.
- 25 8. After drying, filling the frit into the ball mill and grinding, preferably to about 10,000 revolutions.
 - 9. Sifting the ground frits through a sieve, preferably having 100 µm mesh size.

To measure opalescence and transparency of the opal ceramic, it should be noted that 3 grams of the powdery opal ceramics were compacted in a press to form a round blank and these were sintered together in a dental vacuum baking furnace at the same temperature as in Test 13 of 950°C. The round blank thus obtained has a thickness of about 2.5 mm. In the case of opalescence, these round blanks appear orange/yellow with transmitted light since the unscattered long-wave light catches the eye. On the other hand, when looking at it against a dark background, the round blank appears bluish, since the more strongly scattered short-wave light is seen in this case.

This phenomenon can be determined quantitatively with a spectrophotometer. For this purpose, the L*, a*, b* values were measured in transmission and in reflection on a black base in the photometer of, for example, the Minolta corporation (CM-3610d), whereby a 2° observer and standard light D65 are required. In the L*, a*, b* colour system, a positive b* value represents the yellow part of the light, on the other hand, a negative b* value represents its blue part. The higher the absolute amount, the more intense the colour.

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Accordingly, the opalescent round blanks thus produce positive b* values during transmission and negative b* values during reflection. The more the two b* values deviate from one another, the strong the opalescence.

5 Moreover, the L* value measured in transmission can be used as a measure for the transparency of the round blank.

Aesthetically satisfying results in dental restoration are obtained with opal ceramics whose round blanks have a Δb^* of at least 25 and L* (transm.) of at least 75.

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Patent Claims

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Opalescent Glass Ceramic

- An opalescent glass ceramic, in particular an opalescent glass ceramic as a dental material or as an additive to or component of dental material, comprising at least the components SiO₂, Al₂O₃, P₂O₅, Na₂O, K₂O, CaO and Me(IV)O₂, characterized in that the opalescent ceramic is devoid of ZrO₂ and TiO₂, that the glass ceramic has a Me(II)O content of less than 4% by weight and that the Me(IV)O₂ content is 0.5 to 3% by weight.
- The opalescent glass ceramic according to claim 1, characterized in that
 Me(IV)O₂ is composed of 0 1% by weight CeO₂ and 0 2.5% by weight SnO₂.
- The opalescent glass ceramic according to claim 1, characterized in that the Me(II)O content is 2 - 3.5% by weight, in particular 2.5 -3% by weight.
- The opalescent glass ceramic according to any one of the claims 1 to 3, characterized in that the glass ceramic contains the following components:

Component	% by weight
SiO ₂	55 - 62
Al ₂ O ₃	13 - 17
B ₂ O ₃	0 - 2
P ₂ O ₅	1.5 - 3
Li ₂ O	0 - 2
Na ₂ O	7 - 12
K ₂ O	8 - 12
MgO	0 - 2
CaO	1 - 4
BaO	0 - 2
Tb ₂ O ₃	0 - 3
Me(IV)O ₂	0.5 - 3

the indicated amount of Me(IV)O₂ being composed of 0 - 1% by weight CeO₂ and 0 - 2.5% by weight SnO₂.

5. The opalescent glass ceramic according to any one of the claims 1 to 3, characterized in that

% by weight Component 58 - 60 SiO₂ 14 - 15 Al₂O₃ P_2O_5 2.3 - 2.6 9.5 - 10.5 Na₂O K₂O 9 - 10CaO 2.8 - 3.0 SnO₂ 1.3 - 1.6 CeO₂ 0.3 - 0.4 0 - 2.0 Tb₂O₃

the glass ceramic contains the following components:

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The opalescent glass ceramic according to at least one of the preceding claims, characterized in that
 CeO₂ and/or Tb₂O₃ are fused to obtain a fluorescent property.

- The opalescent glass ceramic according to at least one of the preceding claims, characterized in that
 the glass ceramic has a thermal expansion coefficient (TEC) in the range of 9.0 13.5 x 10⁻⁶/K, in particular 10.5 -12.0 x 10⁻⁶/K.
- 8. A method for producing an opalescent glass ceramic according to any one of the claims I to 7, in particular an opalescent glass ceramic as a dental material or as an additive to or component of dental material, comprising at least the components SiO₂, Al₂O₃, P₂O₅, Na₂O, K₂O, CaO and Me(IV)O₂, characterized in that the method comprises the following procedural steps:

the method comprises the following procedural steps:

- weighing in and mixing the components with a mixing ratio according to one of the claims 1 to 6;
- melting the mixture in a furnace;
- quenching the molten mass coming out of the furnace in a water bath and subsequent drying;
- grinding the frit thus obtained in a mill;
- tempering the frit;
- after drying, filling the frit in a mill and grinding the frit;
- sifting the ground frit through a sieve, the sieve opening forming the end.

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9. The method according to claim 8, characterized in that

the tempering of the frit is carried out in the following manner:

- stacking the ground frits on quartz-coated fire-clay plates,
- placing the fire-proof plates in a furnace, e.g. an electric furnace, heated to a temperature T with $850^{\circ}C \le T \le 1000^{\circ}C$,
- removing the plates from the furnace after a time t with 30 min \le t \le 60,
- quenching the melted frit cakes in a water bath.
- The method according to claim 8 or 9, characterized in that the components are mixed in a gyro mixer.
- The method according to at least one of the claims 8 to 10, characterized in that the mixture is melted in a preferably gas-heated drip-feed crucible furnace.
- The method according to at least one of the claims 8 to 11, characterized in that after drying, the frit is filled into a ball mill and ground with about 10,000 revolutions per minute.
- 13. The method according to at least one of the claims 8 to 12, characterized in that the ground frit is preferably sifted through a sieve having a mesh size M in the range of 80 μm ≤M ≤ 120 μm, preferably M ≠ 100 μm.
- 14. The method according to at least one of the claims 8 to 13, characterized in that the fusing is produced by heating the granulated material to 870 to 970°C.
- 15. The method according to at least one of the claims 8 to 14, characterized in that the thermal expansion coefficient (TEC) is set to a value $9.0 \le \text{TEC} \le 13.5 \times 10^{-6}/\text{K}$ by the K₂O content.
- 16. The method according to at least one of the claims 8 to 15, characterized in that the baking temperature of the opalescent glass ceramic is controlled by the proportions of B₂O₃, Li₂O and Na₂O and is preferably in the range of 870°C to 970°C.
- 17. Use of the opalescent glass ceramic according to at least one of the preceding claims as a dental material or as an additive to or component of dental material.

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- 13 -The use according to claim 17, wherein the opalescent glass is a component of inlays, 18. onlays, bridges or crowns.