Research Article

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A multi technique study of a new lithium disilicate glass-ceramic spray-coated on ZrO$_2$ substrate for dental restoration

https://doi.org/10.1515/bglass-2017-0004
Received May 05, 2017; revised Jul 07, 2017; accepted Aug 09, 2017

Abstract: An alkali niobate-silicate veneer ceramic for ZrO$_2$-based dental restoration was developed and characterized for its physical properties and structure. The properties were adjusted for dental applications. The new lithium disilicate glass-ceramic VBK (sold as cerafusion or LiSi) can easily be applied by spray coating to any individually formed ZrO$_2$-matrix and needs only one final tempering treatment. The surface of the glass-ceramic is very smooth. The color of the already translucent glass-ceramic can be adjusted to that of individual natural teeth. The structure of the glass-ceramic was studied by XRD and Raman spectroscopy as a function of heat-treatment and of spatial variations within the material and at its interfaces. ToF SIMS, SEM and thermal analysis techniques were applied to investigate the crystallization behavior and surface-interface reactions. XRD and Raman spectroscopy identified different crystalline phases in the amorphous glass matrix including Li$_2$Si$_2$O$_5$, Li$_2$SiO$_3$, Na$_x$Li$_{(1-x)}$NbO$_3$ and Na$_3$NbO$_4$. The Raman spectrum of the amorphous matrix is dominated by the vibrational activity of the highly polarizable niobate units with a prominent feature at 865 cm$^{-1}$, assigned to Nb-O stretching in NbO$_6$ octahedra, which have non-bridging oxygen atoms and are connected to the silicate matrix rather than to other niobate polyhedra.

1 Introduction

Dental restoration is still an expanding market, since demography together with an increasing awareness of health and aesthetical issues drives the demand for ever improved materials. When discussing the current state of the art in dental restoration based on all-ceramic materials, it is essential to distinguish between framework ceramics and veneer ceramics [1–6]. Furthermore, the interaction between the substrate and the veneer ceramic is critical in applications of any composite material.

Modern dental restoration started to take off with the development of high performance ceramics at the end of the 1990s and intensified substantially with the development of CAD/CAM – techniques [3, 7–10]. Today, different routes for processing are employed by the industry for all ceramic dental restoration [1, 3, 11–14]. The development of new ceramics for dental restoration demands not only a high mechanical performance [15] but also aesthetical and health aspects need to be considered. Thus, important parameters include the minimization of chipping and wear, which can be achieved by: (1) a high flexural and tensile strength, (2) a high crack resistance, and, for composites materials, (3) a well-adjusted coefficient of thermal expansion and (4) decreasing the thickness of the veneer layer. Health aspects include: (5) biocompatibility, (6) non-toxicity and (7) high chemical stability; while optical requirements include: (8) translucency and (9) a high vari-
ability in coloring, in order to fulfill highest aesthetical demands for overall perception [1, 7, 16].

So far, a limited variety of framework ceramics has been used for dental restoration: glass-ceramics, infiltration ceramics, aluminum-oxide strengthened glass-ceramics, and aluminum-oxide or yttrium-stabilized zirconium-oxide [4, 17–19]. The latter, yttrium-stabilized tetragonal zirconium oxide (TZ3Y), is used as substrate material in the current study [18, 19]. The veneering ceramics for dental restorations which were recently developed by the Fraunhofer Institute (IKTS-HD), utilize an yttrium-stabilized ZrO$_2$ framework ceramic (TZ3Y), in combination with a thin layer of veneer ceramic made from powdered glass of the lithium disilicate (LDS) system which can be spray-coated on the sculpted framework [18–22].

Of all the substrate and veneer materials for dental restoration studied systematically by the IKTS-HD [18, 19, 21, 22], the most promising approach for reduced incidents of chipping was subsequently developed further in collaboration with the Elaboro GmbH and finally transferred into production (Cerafusion and LiSi). In order to pass all stages from development into production, the material had to stand out in many quality aspects. Concerning the framework ceramic, TZ3Y has a high chemical stability, is translucent, and is not known for any allergenic reactions or other adverse health risks. The combination of such favorable mechanical and aesthetical aspects, render ZrO$_2$ based substrate ceramics an ideal material for dental restoration.

In this paper, we present and discuss the preparation of a spray-coated veneer ceramic and its characterization based on Raman spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The formation process from glass to the final glass-ceramic product is discussed for different temperature treatments. The effect of varying Li$_2$O levels on the glass-ceramic’s topology is also considered. Furthermore, supportive information is given from thermal analysis, mechanical testing, and ion diffusion between the veneer ceramic and the ZrO$_2$ based substrate as studied by SEM and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF SIMS). Characteristic properties and a structural analysis of the veneer ceramic during sintering is also given, as well as structural analysis at the interfaces of the glass-ceramic with the framework ceramic and of the glass-ceramic at the outer tooth’s surface with air or later the oral milieu. As will be shown in this study, all named problems concerning veneer ceramics seem to have been resolved most favorably for the LDS-based ceramic VBK 228.

2 Experimental

2.1 Glass-ceramic preparation conditions

The veneer ceramics of the current study are based on lithium silicate compositions with varying amounts of additives ranging from borates to niobates. VBK belongs to the niobate-containing lithium disilicate glass-ceramic series, where the compositional ranges selected for their most promising properties for dental applications are in mol%: SiO$_2$ (53 – 69%) · Al$_2$O$_3$ (0.5 – 3.5%) · B$_2$O$_3$ (0.5 – 4.0%) · Li$_2$O (19 – 38%) · Na$_2$O (2 – 6%) · Nb$_2$O$_5$ (2.0 – 4.5%) · ZrO$_2$ (0.2 – 2.0%) [20]. Powders of the raw materials (SiO$_2$, Li$_2$CO$_3$, Na$_2$CO$_3$, Al(OH)$_3$, B$_2$O$_3$, H$_3$BO$_3$, Nb$_2$O$_5$, ZrO$_2$) were mixed and melted into a glass. The glass melt was subsequently fritted and pulverized to a grain size $d_{50} < 10 \, \mu$m. From this glass powder, a dispersion was prepared which was then applied to a ZrO$_2$ substrate by spray coating. For the discussed experiments, the mixture was sintered at variable times and temperatures, as explained in more detail in the following sections. For spray-coating in production, the dispersion was optimized by the addition of organic solvents and a propellant.

For the current study, the composites were heat-treated for one hour at temperatures varying from 600 to 920$^\circ$C. Test slabs of different compositions and various heat-treatments were used for most of the experiments discussed in detail in this paper.

In order to generate the final dental replacement products as those shown in Figure 1, two different procedures of processing can be applied. In the first, after spray-coating, a 10 min tempering step is applied to generate the LDS glass-ceramic, selecting 890$^\circ$C to 905$^\circ$C. This temperature suffices to bond the veneer ceramic to the ZrO$_2$ substrate, but is not so high as to re-melt the lithium disilicate glass-ceramic. In the second procedure, a tempering step of 5 min at 820$^\circ$C is followed by an additional tempering step of 5 min at 920$^\circ$C. This additional high temperature tempering causes a temporary and partial re-melting of the LDS crystals and enhances bonding of the veneer to the framework ceramic. This second procedure is favoured in actual applications. As apparent from the photographs shown in Figure 1, the surface of the LDS veneer (VBK 228) is very smooth after thermal treatment of the spray-coated glass powder. The veneer can be applied to any individually formed ZrO$_2$ substrate by spraying and was proven to be a very good material for thin film coatings of approximately 8 $\mu$m thickness.
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Figure 1: Photographs of dental VBK coatings based on the lithium disilicate veneer ceramic VBK 228: (a) bridge, (b) veneer cap and (c) crown (mirrored). The anatomical design of the ZrO$_2$-framework was generated first by CAD/CAM [23], before coating by spraying the framework with VBK228 which was transferred into a lithium disilicate glass-ceramic by a subsequent heat treatment for 10 min at 890$^\circ$C, a spray-coating technique which was developed in cooperation of IKTS and Elaboro GmbH (photo: www.elaboro.net).

2.2 Characterization techniques

Differential thermal analysis (DTA) curves were obtained, from the glass powder from which the veneer is derived, by thermo-mechanical analysis, TMA, using a Setaram S.A., TG-DTA 92 – 1750, instrument. A heating rate of 5 K/min was employed. The error of the transition temperature, determined as onset of the DTA curve, and of the crystallization events, was about ±5$^\circ$C. The instrument also gave the mass loss during heating of the samples (thermogravimetric analysis, TGA); the variations in the samples mass were found to be ±1.3% when heating from room temperature to 1500$^\circ$C. The coefficients of thermal expansion (CTE) of the TZ3Y substrate and the lithium disilicate veneer ceramic VBK228 were determined by dilatometry.

For X-ray diffraction (XRD) measurements a Bruker AXS, D8 Advance instrument was utilized, using a Cu-cathode and a 1-dimensional detector LynxEye®. Quantitative determination of the crystal phases by Rietveld analysis was performed with the commercial software AutoQuan Version 2.7.1.0® using structure data of ICSD. For samples heat-treated at 890$^\circ$C or more, no cristobalite was detected.

Scanning electron microscopy (SEM) was conducted on a FEREM Ultra 5+ instrument from Zeiss, equipped with energy-dispersive X-ray (EDX) spectroscopy capabilities for quantitative elemental analysis (linescan). Transmission electron microscopy (TEM) and ToF SIMS results were provided from the Fraunhofer-Center for Applied Microstructure diagnostic (CAM) of the Fraunhofer Institute of Material Mechanics (IWM). For high resolution TEM measurements, two samples were joined to a sandwich, which was then mechanically ground and polished before dimple-grinding and ion beam thinning turned them into TEM samples. For the prevention of electrostatic charging, the sample was coated by carbon vaporization.

For ToF SIMS measurements, an ionof TOF-SIMS5-100 Instrument was used. An embedded cross-section of the sample was partially covered with conducting graphite for high mass and high spatial resolution at the interface of the substrate with the lithium disilicate glass-ceramic. Before each measurement, the area of analysis was flashed for 10 seconds with low energy O$^{2+}$ ions (500 eV). For the high current bunched mors, Bi$^+$ ions were used as primary ion species, under positive polarity, the cycle time was 100 µs, the analysed area was 500 × 500 µm$^2$ each, and the number of scans was 50. Charge compensation was accomplished by a low energy electron flow/current. The same parameter were used for the burst alignment modes, however theanalysed area was (500 × 500 µm$^2$)/(200 × 200 µm$^2$), averaging over 20 scans.

Raman spectra were acquired on an inVia Renishaw confocal Raman microscope, equipped with the 514.5 nm excitation line of an Ar$^+$ laser and an objective of x50 magnification. All measurements were performed at room temperature in the range 200 to 1500 cm$^{-1}$ and with 2 cm$^{-1}$ resolution. Polarized Raman spectra were recorded on the same instrument. A x100 objective was used for linescans, like the closely spaced Raman spectra shown in Figure 6.

Mechanical testing for flexural strength was performed according to the European standard EN 843-1, using a three point bending set-up. The scattering of these measurements is given by the Weibull parameter, e.g. m=8.3 for a sample heat-treated for 30 min 890$^\circ$C.

The tensile strength was used as a measure for the adhesive strength between VBK 228 and TZ3Y. Tensile strength measurements were conducted at the University of Ulm, Germany, on a universal testing machine (Z010, Zwick/Roell, Ulm, GER).

Finally, the chemical stability of the glass-ceramic was tested according to DIN EN ISO 6872.

3 Results and discussion

Table 1 lists selected properties of the LDS-based veneer ceramic VBK228 and of the Y- stabilized ZrO$_2$ substrate
Table 1: Selected properties of the LDS-based veneer ceramic VBK228 and of the Y-stabilized ZrO$_2$ substrate (TZ3Y), with their values determined experimentally according to the procedures listed in the experimental section.

<table>
<thead>
<tr>
<th>Selected parameters</th>
<th>lithium disilicate veneer ceramic (VBK 228)</th>
<th>TZ3Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal expansion coefficient CTE (25-500°C)</td>
<td>9.8±0.2 × 10^{-6}/K</td>
<td>10.5 ±0.2 × 10^{-6}/K</td>
</tr>
<tr>
<td>Chemical solubility (DIN EN ISO 6872)</td>
<td>23.7 ± 3.7 µg/cm$^2$</td>
<td>6.1±1 µg/cm$^2$</td>
</tr>
<tr>
<td>Flexural strength, $\sigma_f$ (EN 843-1)</td>
<td>138 MPa</td>
<td>&gt;1000 MPa</td>
</tr>
<tr>
<td>Weibull-Parameter, m</td>
<td>8.3</td>
<td>9</td>
</tr>
<tr>
<td>Tensile strength VBK228/TZ3Y</td>
<td>20 MPa (±4.5 MPa)</td>
<td></td>
</tr>
</tbody>
</table>

(TZ3Y) used in this study. The chemical stability places VBK228 into class 1, which is very satisfactory (see Table 1).

Variants of translucent ZrO$_2$ substrate or dental replacements allow for individual coloring for highest aesthetic demands [1]. Currently, some commercial translucent LDS framework ceramics might still have an advantage in this respect, especially when discussing the anterior (front) tooth area. In both cases, CAD/CAM processing of translucent LDS ceramic, as well as translucent ZrO$_2$ substrate, requires a two-step sintering process [2].

### 3.1 Selected mechanical properties

The measured value of ca. 20 MPa for the adhesive strength of the VBK glass-ceramic to the ZrO$_2$ substrate is significantly higher than for conventional veneer ceramics used in dental restoration. For example, measurements of the tensile strength, conducted under identical conditions using TZ3Y as substrate, gave the following values for commercially available dental products: 5 ± 1.5 MPa for a sintered leucite glass-ceramic used for veneering that was applied on TZ3Y, and 6 ± 2.8 MPa for a fluor-apatite based veneer ceramic applied on TZ3Y. Thus, the new developed LDS veneer ceramic combination of VBK 228 on TZ3Y has a three to four times better tensile strength and subsequently much better adhesive properties than conventional veneer ceramics.

Another important parameter for the characterization of framework ceramics is their flexural strength, $\sigma_f$. Ceramics based on lithium disilicate exhibit, for example, $\sigma_f$ values between 300 MPa to 400 MPa [7, 24]. In comparison, yttrium-stabilized zirconium dioxide has a flexural strength of more than 900 MPa [5, 7, 8, 17, 18, 25]. This makes TZ3Y the predestined material for framework ceramics [14, 18]. Yttrium-stabilized tetragonal zirconium dioxide has a Vickers hardness of more than 1250 MPa [13, 17, 18, 26, 27]. The hardness of natural tooth enamel is lower, closer to 275-550 MPa [10, 26, 27], and thus, comparable to the hardness of glasses and glass-ceramics [28]. Abrasion depends foremost on the smoothness and only secondarily on the difference in hardness, therefore, the observed difference in hardness between TZ3Y and natural teeth is only a minor factor. However, other requirements listed for dental restoration, including aesthetic demands, are not fulfilled by TZ3Y and thus, a veneer or coating is required. Coating of a framework ceramic with a veneer ceramic allows not only to copy the multitude of natural occurring colorations, but can also be used for adjusting the relative hardness of the ceramic to the hardness of natural teeth [22, 29]. In multicomponent systems, the adhesive strength is just as important as the flexural strength.

Conventional used fluor-apatite, leucite or feldspar based layered veneer ceramic materials exhibit a flexural strength $\sigma_f$ ~ 80 to 120 MPa [5, 7, 24]. Leucite, for example, displays an unsatisfactory failure which is revealed in a high incidence of fracture or chipping [3, 8, 12, 14, 15, 25, 28, 30–33]. The strong increase of chipping with time, as discussed in reference [33] for glass-ceramic veneers on ZrO$_2$ substrate indicates that many parameter and fatigue mechanisms contribute to eventual failure.

In order to select a corresponding veneer ceramic, its characteristics are required to fit those of the framework ceramic or substrate, for which TZ3Y was chosen in the current study. The thermal expansion coefficient of the veneer ceramic should be similar to that of the substrate, with ZrO$_2$ having CTE=10.5 × 10^{-6}/K [10, 34]. The CTE of glass-ceramics depends on both the CTE of the crystalline as well as the CTE of the vitreous phase and can therefore be adjusted over a significant range e.g. from 10 − 11×10^{-6}K^{-1} in LDS glass-ceramics [35]. The measured CTE value of the VBK228 glass-ceramic is 9.8 × 10^{-6}K^{-1}, which is comparable to the CTE of the ZrO$_2$ substrate.
As mentioned earlier, lithium disilicate based glass-ceramics in bulk form are known for their high flexural strength of $\sigma_{fs} \approx 350$ MPa, but are additionally translucent, have a high chemical stability and are nontoxic [36]. It should be noted, that the flexural strength of a glass-ceramic derived from bulk crystallization of a compact glass differs significantly from a glass-ceramic derived from surface crystallization of a glass-powder [6]. The newly developed lithium disilicate based thin layer veneer ceramic exhibits still a relative high flexural strength of 138 MPa. More importantly, because of its preparation in extremely thin layers of only 8 µm, the overall strength of the zirconia substrate dominates and through its excellent adhesiveness to zirconium oxide the incidence of chipping is greatly reduced, culminating in excellent surface qualities [20–22].

3.2 Thermal properties

Thermal properties, such as thermal events occurring upon heating the veneer material are depicted in Figure 2 for the case of VBK228 glass-powder. TGA indicates a mass loss of less than 1.5% when the material is heated up to 1500°C. DTA results reveal that the transition temperature of the glass matrix, $T_g$, measured at the onset of the endothermic peak, is 480°C. Two crystallization events are apparent with maxima at 700°C and 740°C, due to the formation of Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$ respectively, as confirmed by XRD (see section 3.3). The melting temperature was determined at 925°C, with the onset at 890°C. As noted in section 3.4., crystallization will alter the composition of the vitreous and crystalline phases and, therefore, the plot shown in Figure 2 should vary for partially crystallized samples as well as when employing different heating rates.

3.3 Influence of temperature on crystallization (XRD patterns and SEM images)

X-ray diffraction patterns of differently heat-treated VBK228 glass-ceramics are depicted in Figure 3. In accordance with the DTA data discussed in section 3.2, lithium disilicate (Li$_2$Si$_2$O$_5$) accounts for a substantial fraction of the crystals formed in all differently heat-treated samples. A detailed examination shows several strong reflections of differently oriented Li$_2$Si$_2$O$_5$ crystals ($2\theta = 16.7, 23.8, 25.0,$ and 38.0 deg.) for the samples treated for one hour at either 760°C, 840°C, or 890°C (Figures 3a to 3c). Only the sample heated for 1 hour at 905°C, see Figure 3d, shows solely the diffraction pattern of Li$_2$Si$_2$O$_5$ with a preferred growth along the c- and to a lesser degree the a–axis ($2\theta = 12.2$ and 24.5 deg.). Characteristic Bragg peaks for lithium meta-silicate Li$_2$SiO$_3$ are additionally observed ($2\theta = 19.2$ and 33 deg.). Furthermore, sodium niobate, Na$_3$NbO$_4$ (near $2\theta = 16.5$ deg.) and mixed lithium–sodium niobate, Na$_2$Li$_{(1-x)}$NbO$_3$ phases (near $2\theta = 23$ deg.) were included as minor components in the quantitative XRD analysis for samples heat-treated at 890°C. Small traces of alkali borates might further account for the remaining weak reflections.

The strong reflections near $2\theta = 30$ and 60 deg, are typical for tetragonal ZrO$_2$ diffraction peaks. While a similar pattern might be expected for cristobalite, it is important to note that the latter also shows a weaker reflection at $2\theta = 21.8$ deg., which is absent for tetragonal ZrO$_2$. While this reflection is present for the studied samples treated at lower temperatures, it is non-existent in the diffractograms of the samples treated at 890 or 905°C. Therefore, no cristobalite is present in the two glass-ceramics treated at the highest temperatures, which are also the relevant samples for dental applications.

The relative fraction of each crystal type was determined by Rietveld analysis and the values are listed in Figure 3. Cristobalite is a minor species for low temperatures, with its relative amount decreasing from 8% at 760°C to 3% at 840°C. For heat treatments at higher temperatures,

![Figure 2: Differential thermal analysis (DTA) of the glass powder from which the lithium disilicate veneer ceramic VBK228 originates. Thermal events, such as the glass transition temperature $T_g$ (onset of endothermic peak), crystallization temperatures $T_c$ for two different lithium silicates and the melting temperature $T_m$, are highlighted in the graph.](image-url)
Figure 3: XRD patterns of VBK ceramics heat-treated for one hour at different temperatures. The diffraction peaks of the main crystal fractions are indicated according to the labels in the figure. TZ3Y overlays most SiO$_2$ (cristobalite) peaks other than the one labeled with (*). On the right hand side, the corresponding SEM photographs of cross-sections of broken samples are depicted. For the sample heat treated at 905°C, the photograph was taken after 10 min at 905°C. The TZ3Y substrate and, when applicable, the ceramic-air interface is indicated in the photographs. Note the higher magnification of the SEM images taken at the air-VBK interface of samples heat treated at 890 and 905°C.

cristobalite is below the detection limit. Lithium disilicate is the majority species with 83% content in the sample treated at 760°C, ca. 92% at 840 and 890°C treatment, and 100% after heat treatment at 905°C. Niobates were only detected after heat treatment for 1 hour at 890°C, with a relative fraction of 2% for the mixed Na$_x$Li$_{(1-x)}$NbO$_3$ crystals and 5% for the sodium niobate crystals Na$_3$NbO$_5$.

3.4 Impact of variations in the LiO$_2$:SiO$_2$ ratio on crystallization (SEM)

In addition to Figure 3, which shows scanning and transmission electron micrographs of differently heat-treated glass-ceramics, Figure 4 shows additional micrographs of the impact variations in the Li$_2$O:SiO$_2$ ratios have on the morphology of the glass-ceramics. In these experiments, the remaining components of the original glass frit are kept at comparable levels. As apparent from the TEM pho-
Figure 4: TEM photographs of glass-ceramic samples with varied Li$_2$O:SiO$_2$ ratios after 10 minutes heat treatment at 890°C: (a) VBK 228 with Li$_2$O:SiO$_2 = 1:2.6$ (identical in composition to Figure 3), a decreased Li$_2$O and increased SiO$_2$ fraction compared to the stoichiometric lithium di-silicate of 1:2, and (b) a VBK 229 sample with increased Li$_2$O fraction and a ratio of Li$_2$O:SiO$_2 = 1:1.4$. Li$_2$O:SiO$_2$ ratio of 1:2.6. For lithium disilicate based glass-ceramics, close attention has to be paid to the critical crystal growth rate during crystallization of the compacted materials or powders. The swiftness of crystallization, in conjunction with the impact the crystallization process has on the viscosity of the remaining material, needs to be controlled carefully during production. As shown by Burgner and Weinberg, the maximal speed of crystallization of a lithium silicate based glass system is $U_{900°C} \approx 10 \mu m/sec$ [37, 38]. Due to the high crystallization rate, each grain in a powdered glass-ceramic crystallizes completely within one second. The resulting increase in the viscosity causes a spontaneous decrease in the speed of any further sintering reactions between neighboring grains. These observations give rise to several principal obstacles in the preparation of LDS-based veneer glass-ceramics. The first one concerns the bonding strength between the grains of the powdered glass-ceramic. The second question concerns the adhesion of the glass-ceramic to the ZrO$_2$-substrate. Finally, the third important question concerns the surface quality of the dental veneer glass-ceramic. Several aspects along these lines are considered in the following sections.

3.5 Interface between ZrO$_2$ substrate and glass-ceramic (Line Scan SEM, ToF SIMS)

The interface between the TZ3Y-substrate and the glass-ceramic was further analyzed quantitatively by energy dispersive scanning electron microscopy (SEM-EDX) and by
time of flight secondary ion mass spectroscopy (ToF SIMS). As depicted in Figure 5, a noteworthy diffusion of zirconium up to 4 µm into the glass-ceramic is observed. It is also apparent, that Nb is absent from lithium disilicate crystals, which can be identified by a sharp increase in Si spikes (Figure 5).

SEM-EDX is not sensitive enough to show the diffusion of most elements other than niobium and zirconium. However, the linescan, as indicated by the white line in Figure 5, shows not only variations in the ion profiles between the Zr₂O-substrate and the glass-ceramic, but also reflects the variations in composition between the vitreous matrix compared to the dark crystalline inclusions. The crystals are rich in silicon, but poor in niobium. From XRD studies, this would indicate the formation of Li₂Si₂O₅ crystals, as expected for LDS. Niobium and other ions aggregate in the remaining glassy phase which in turn impacts the viscosity of the glass phase favorably.

ToF-SIMS confirmed the presence of traces of Li⁺ and Na⁺ in the ZrO₂ substrate up to a depth of 2 µm. Additionally, at the interface between the vitreous matrix and the crystalline LDS, a decrease of lithium ion content is observed, as these ions are incorporated into the crystals. Sodium and niobium ions accumulate in the area enclosing the Li₂Si₂O₅ crystals.

Heat treatment at 905°C causes an even stronger depletion of Li-ions from the glass matrix, as these are incorporated in the now formed Li₂Si₂O₅ crystals.

3.6 Raman spectroscopy

Raman spectroscopy was employed in order to investigate structural aspects of the glass-ceramic. This includes not only the differently formed crystals, but also the vitreous area around the crystals. Moreover, the interface between the TZ3Y substrate and the glass-ceramic, as well as the outer surface of the glass-ceramic warrant special interest in regard to glass formation and to structural evolutions in the glass-ceramic.

Figure 6a depicts selected Raman spectra along a line at the cross section from the TZ3Y substrate to glassceramic interface of a VBK228 sample heat-treated at 890°C for 10 min. The Raman spectrum measured at x=7.5 µm reveals the characteristic bands of tetragonal ZrO₂ at 145, 261, 317, 465, and 642 cm⁻¹ [39, 40]. Mapping of the substrate-veneer ceramic interface shows an intensity decrease of the bands assigned to tetragonal ZrO₂, and the progressive development of a broad band peaking around 855 cm⁻¹. As apparent from Figure 6b, no crystals are present in this transection close to the interface. Hence, the Raman spectra of the veneer ceramic reflect the vitreous nature of the probed material. Besides the broadness of the 855 cm⁻¹ band, the vitreous character of the veneer material is manifested also by a broad Raman envelope from about 950 to 1100 cm⁻¹.

We note that the observed ZrO₂ Raman signal, which remains visible for measurements even at points more than 5 µm into the veneer glass-ceramic (Figure 6), might be due to the accidental sampling of underlying ZrO₂, which could be probed if the cut of the glass-ceramic deviates somewhat from perpendicularity. Furthermore,
the polarizability of Zr-O bonds is larger than that of Si-O bonds because of the much higher polarizability $\alpha$ of the Zr$^{5+}$ ion compared to Si$^{4+}$, with $a(Zr^{5+}) = 0.37 \text{ Å}^3$ and $a(Si^{4+}) = 0.033 \text{ Å}^3$ [41, 42]. Since the Raman intensity of a vibrational mode is proportional to the square of the polarizability derivative with respect to the normal coordinate of the mode (e.g., bond stretching) [43], the Raman scattering cross section of Zr-O related vibrations is predictably significantly larger compared to silicate related bonds. Consequently, even relatively small numbers of Zr-O bonds in a silicate matrix are expected to show significant Raman signals. A similar effect is expected for the Nb-O bonds, since $a(Nb^{5+}) = 0.262 \text{ Å}^3$ [42], so that both Zr- and Nb-containing structural entities will contribute strongly to the Raman spectra, even when only present in small amounts [44, 45].

As for the origin of the broad Raman features at 1075 cm$^{-1}$ and 855 cm$^{-1}$ in Figure 6a, we note that Nb$^{5+}$-containing silicate glasses exhibit Raman bands at around 1000 to 1100 cm$^{-1}$ and 800-900 cm$^{-1}$, which have been associated with the stretching modes of Si-O and of Nb-O bonds, respectively [46]. Characteristic Si-O stretching modes in crystalline Li metasilicate, Li$_2$SiO$_3$, and Li disilicate, Li$_2$Si$_2$O$_5$, where the silicate tetrahedra have two (Q$^2$) and three (Q$^3$) bridging oxygen ions respectively, have been measured at 976 and 1101 cm$^{-1}$ [46–50]. The nomenclature Q$n$ denotes SiO$_4$-tetrahedra with $n$ bridging and 4-$n$ non-bridging oxygen atoms. On the other hand, the Raman band at 855 cm$^{-1}$ in Figure 6a can be associated with niobate units with non-bridging oxygen atoms. The large bandwidth of this band is indicative of Nb-O stretching in distorted NbO$_6$ octahedra, and this may arise from their bonding to more silicate than niobate entities [45]. This proposed assignment is also supported by the available literature including reviews on Raman spectra of structurally well-defined niobate compounds [46, 51–55].

For example, Cardinal et al. [51, 52] showed that the introduction of Nb$_2$O$_5$ to borophosphate glasses leads to the formation of distorted isolated NbO$_6$ octahedra (900 cm$^{-1}$), and for higher Nb$_2$O$_5$ concentrations to corner sharing NbO$_6$ octahedra in chain formations (830 cm$^{-1}$). For very high Nb$_2$O$_5$ levels, a Raman band was measured at 650 cm$^{-1}$ and assigned to a 3D framework of connected niobate octahedra.

It is generally observed that the Nb-O stretching modes of octahedral NbO$_6$ groups shift from around 600 cm$^{-1}$, for NbO$_6$ octahedra connected with more than three other NbO$_6$ entities, to increasingly higher wavenumbers as more niobate connections are replaced by silicate species [46, 51, 52, 55, 56]. Kioka et al. [53] observed a band near 870 cm$^{-1}$ in the Raman spectra of K$_2$O-Nb$_2$O$_5$-SiO$_2$ glasses, similar to the one shown in Figures 6 to 8, and Lipovskii et al. [54] measured a related feature for low Nb$_2$O$_5$ concentrations in silicate glasses. However, the presence of NbO$_4$ tetrahedra cannot be fully excluded, since these units also show Raman bands near 850 cm$^{-1}$ and are known to exist at low concentrations in silicate glasses [45, 55].

Figure 7 shows the Raman spectra measured at selected points of the heat-treated (10 min at 890°C) VBK228 glass-ceramic to probe crystalline as well as vitreous parts of the material. The probed crystals can be identified by comparison with the Raman spectra of pure crystalline compounds. Thus, the voluminous spherical crystal of Figure 7a is lithium disilicate (Li$_2$Si$_2$O$_5$) as all characteristic bands (in cm$^{-1}$) are present: 1107 (vs), 1033 (v-w), 934 (m), 785 (m), 642 (w), 551 (s), 519 (w, sh), 465 (m), 414 (vs), 375 (s), 317 (w), 285 (v-w, sh), 264 (s), 246 (w), 235 (w), 193 (s), 152 (vv) (w: weak, m: medium, s: strong intensity, v: very, sh: shoulder) [37, 49]. The same Raman fingerprint of Li$_2$Si$_2$O$_5$ can be distinguished in all other spectra of Figures 7b to 7e, although these are often partially overlaid by broader bands from the glassy matrix (Figures 7b-7d) or coexist with additional sharp bands from other compounds (Figures 7c and 7e). In Figure 7b and 7d, the Raman bands of the Li$_2$Si$_2$O$_5$ crystal are probably sampled from below the vitreous matrix on which the Raman beam was focused. As discussed above, the broad band at 865 cm$^{-1}$ in Figure 6 and Figures 7b-7d is typical of the amorphous phase and can be attributed to Nb-O stretching in distorted NbO$_6$ octahedra which are connected to silicate rather than to other niobate units [45, 53, 54, 57]. Such a unit is proposed in Schematic 1a. The origin of the narrow band at 860 cm$^{-1}$ in Figure 7e is discussed next.

The combination of sharpness of the Raman peaks of crystalline Li$_2$Si$_2$O$_5$ with its high volume fraction of 80 to 90% of the crystalline phase makes these peaks so profound in all spectra of Figure 7. Besides the peaks characteristic of the Li$_2$Si$_2$O$_5$ crystal, Figure 7e shows additional sharp peaks at 163 (m), 174 (m), 271 (m), 319 (v-w), 644 (w), 669 (w), 860 (vs) and 1051 cm$^{-1}$ (m). We inspect now the Raman spectra for signatures of the presence of additional prospective candidates among the detected crystalline phases (Figure 3c). Besides the dominating Li$_2$Si$_2$O$_5$ crystalline phase, we check for Na$_3$Li$_4$(NbO)$_7$O$_6$ (including the luzhite mineral Na$_2$NbO$_4$), Li$_3$SiO$_3$, SiO$_2$ cristobalite, and Na$_2$NbO$_4$. Regarding the silicates, the reported Raman activity for both Li$_2$SiO$_3$ [58] and SiO$_2$ cristobalite [59] cannot account for the additional sharp peaks in Figure 7e. Comparison with the Raman spectra of LiNbO$_3$ in single-crystalline [60–63] and polycrystalline [55, 64, 65] forms indicates that the observed additional bands should not be due to LiNbO$_3$. In fact, the strongest high frequency
Figure 7: Raman spectra and corresponding microphotographs of Nb-containing lithium disilicate veneer glass-ceramic (VBK228) measured at: (a) the center of a spherical Li$_2$Si$_2$O$_5$ crystal, (b) the veneer surface or air to glass-ceramic interface, consisting mainly of vitreous material, (c) crystal aggregations giving the signature peaks of Li$_2$Si$_2$O$_5$ (blue crosses) and an additional crystalline phase (red circles), (d) mainly vitreous matrix between crystals (same micrograph as (c)), and (e) Li$_2$Si$_2$O$_5$ crystals (blue-numbered peaks) coexisting with an additional crystalline phase (red-numbered peaks).
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Schematic 1: Proposed connectivity of NbO$_6$-octahedra in the amorphous phase; distorted NbO$_6$-octahedra connected only to silicate units (a, left), and distorted NbO$_6$-octahedra with three NBOs connected to three silicate units (b, right).

Figure 8: Unpolarized (VV+VH), parallel polarized (VV) and cross-polarized (VH) Raman spectra of the vitreous material between the crystals (a), and of crystals (b).

Raman feature of the latter crystal occurs at 630 cm$^{-1}$, $A_1$(TO$_4$) mode, and such a band is not observed in Figure 7. In addition, while the strongest band in Figure 7e occurs at 860 cm$^{-1}$, the LiNbO$_3$ crystal shows a much weaker peak at 878 cm$^{-1}$ with symmetry $E$(TO+LO) [55, 60–65]. In order to examine the possibility that preferential orientation influences the relative Raman intensities of LiNbO$_3$ crystals, we measured polarized (VV) and depolarized (VH) Raman spectra at vitreous areas between crystals (Figure 8a) and at crystal formations (Figure 8b) within the studied material. Preferential orientation would for example result in the disappearance of the polarized 630 cm$^{-1}$ band, while the depolarized band at ca. 860 cm$^{-1}$ would gain intensity. As can be observed in Figure 8a, the entirely symmetric mode of crystalline Li$_2$Si$_2$O$_5$ at 1107 cm$^{-1}$, due to Si-O$^-$ stretching in Q$^3$ units, is strongly polarized as expected, but no polarized band emerges at 630 cm$^{-1}$. Instead, the broad 865 cm$^{-1}$ band of the vitreous phase was found to be strongly polarized. This is also true for the sharp 860 cm$^{-1}$ band in Figure 8b, and this rules against its assignment to a mode of E-type symmetry. All these results taken together support the absence of pure LiNbO$_3$ crystals, as suggested by XRD (Figure 3). Also, the Raman spectrum of the NaNbO$_3$ crystal (lueshite mineral) exhibits relatively sharp and strong peaks at 225, 575 and 865 cm$^{-1}$ and weaker features at 280 and 740 cm$^{-1}$ [64]. We note that the simultaneous absence from Figure 7e of relatively sharp bands at 225 and 575 cm$^{-1}$ suggests the absence of niobate entities similar to those present in the lueshite mineral, i.e. NbO$_6$ octahedra without NBOs.

The second niobate crystal structure identified by XRD is Na$_3$NbO$_4$ (Figure 3), and therefore we discuss here its possible contribution to the Raman spectrum in Figure 7e. Since the Raman spectrum of the Na$_3$NbO$_4$ crystal is not available, we consider reported Raman spec-
tra of the isostructural Li$_3$NbO$_4$ crystal [46, 66]. Its structure consists of NbO$_6$ octahedra which have three non-bridging oxygen (NBO) atoms, while the other three oxygen atoms are shared by three other NbO$_6$ octahedra [66]. The strongest Raman band of Li$_3$NaO$_4$ was reported at 824 cm$^{-1}$ [66] or 840 cm$^{-1}$ [46], and originates from the symmetric stretching mode of such NbO$_6$ octahedra with NBOs. Along these lines, we tentatively associate the broad Raman band at 865 cm$^{-1}$ (Figure 8a) in the amorphous phase and that at 860 cm$^{-1}$ in the crystalline phase (Figure 8b) with the presence of NbO$_6$ octahedra which have NBOs charged balanced by Na$^+$ cations, Nb–O–Na$^+$. Fukumi and Sakka argued that a decreasing number of NBOs in a NbO$_6$ octahedron results in the increase of the Raman frequency in the region above 800 cm$^{-1}$ [46]; this frequency can reach values as high as 900 cm$^{-1}$ [67]. Thus, the results of Raman spectroscopy in Figure 7e are consistent with the presence of Na$_3$NbO$_4$-type crystalline structures and possibly of mixed (Na$^+$, Nb–O–Na$^+$). The strongest Raman band of Li$_2$Si$_2$O$_5$, and Nb–O–Si bonding in NbO$_6$ octahedra in the amorphous phase would also contribute to the band envelop centered at 865 cm$^{-1}$, and thus its broadness indicates the multiple origin of this band [51, 52, 67]. In this respect, we mention a typical problem in earlier literature where the absence of homonuclear Nb–O–Nb bonds was often taken as evidence for the presence of non-bridging oxygen atom, without further discussion if this oxygen atom is actually charge balanced by a modifier cation (e.g., Na$^+$) or, instead, bonded to a less polarizable conventional glass forming cation (e.g., B$^{3+}$, Si$^{4+}$ or P$^{5+}$). We note also, that Nb–O–Na$^+$ bonding might be responsible for the low viscosity of this glass, while the presence of Nb–O–Si bonds might on the other hand be the cause of the good chemical durability of the investigated VBK material.

**4 Conclusions**

The combination of a strongly adhesive and less than 10 µm thick coating of VBK glass-ceramic on a ZrO$_2$ support fulfills high functional and aesthetic demands which are required in dental restoration, while at the same time being very cost effective. In this work, a suspension of lithium disilicate (LDS) glass powder was spray-coated on an anatomical design that is a ZrO$_2$ support that can be individually generated by CAD/CAM. The coated material was found to crystallize to a lithium disilicate glass-ceramic after heat treatment for 10 min at 890°C as shown by XRD and Raman spectroscopy.

SEM and Raman spectroscopy confirmed that an amorphous phase forms on the outer surface of VBK228 upon heat treatment. Alkali ions are needed in the formation of silicate and niobate crystals, thus leaving an alkali poor, chemically stable niobate-silicate glassy phase. Raman spectroscopy was particularly informative for the formation of such a glassy phase by heat treatment, mainly because of its high sensitivity to niobate structural entities due to the high polarizability of the niobium ions. This amorphous niobate-silicate layer has a thickness of only a couple of µm. The results of SEM and Raman techniques were in line with the favorable first visual and tactile impression of the smooth outer surface of VBK228. Preferential orientation of the silicate, Li$_2$Si$_2$O$_5$, and niobate, mainly (Na$_{1-x}$Li)NbO$_4$, crystallites in the thin glass-ceramic layer might further contribute to the smooth feeling. The surface smoothness does not require additional polishing and shows a very high stability against abrasion. The in-built smoothing by the formation of a vitreous layer on the air–veneer interface, in combination with the spraying technique of lithium disilicate glass powders, decreases the manufacturing time of the coating process by a factor of more than four.

Variations of the composition showed that a slight surplus of Li$_2$O over SiO$_2$ is important in order to generate this effect. If more lithium oxide is added, lattice defects, sharp crystal boundaries and inclusions will spoil the desired effect. However, with an excess of SiO$_2$, such as in the favorable ratio of Li$_2$O to SiO$_2$ (1 to 2.6) and through the addition of several mol% Nb$_2$O$_5$, the rapidly crystallizing LDS was found to lead to the formation of a glass-ceramic which bonds strongly to the ZrO$_2$ substrate. It was shown also that interface phenomena of the veneer ceramic VBK228 at the surface with air, or at the interface with the ZrO$_2$ substrate, could be controlled via the composition dependent crystallization reactions.

The new technique presented in this study is actually an intermediate between veneering and spray coating [68]. The described dental veneer ceramic is now commercially available under the trade names LiSi or CeraFusion. The support can be colored already according to the customers’ requirements, with a targeted application of pigments to mimic fissures or other idiosyncrasies. More studies are still required for the optimization of the coloring pigments, explicitly in regard to the impact of these pigments on the adhesiveness of the veneer ceramic to the substrate, the longtime stability and the development of more colors and hues.

**Acknowledgement:** The authors are grateful for the financial support from the *German Bundesministerium für
Wirtschaft und Technologie. Furthermore, they wish to acknowledge the help of many co-workers at the Fraunhofer Institute, including analytics (REM, XRD), and particularly of Dr. Kriegel (Rietveld), A. Montag (Laboratory), A. Hoffmann (melting), and Dr. Schneider (Raman measurements). The authors are also grateful to Prof. Höche (TEM) and Dr. Krause (ToF-SIMS) at the Fraunhofer CAM in Halle, and thank Doris Ehrt for helpful discussions.

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