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Opalescence in dental products[1]

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Abstract

The aim of the investigation was to develop an opal dental glass, to characterize its microstructure and to determine the thermal properties.

It was possible to develop opal glasses derived from the system SiO_2–Al_2O_3–K_2O. The opalescent effect is comparable to that of natural teeth.

During this study it was found that two mechanisms must be controlled: the phase separation in the glass and the minimum surface crystallization at glass grain boundaries within the monolithic sample.

Keywords: Dental glass; Dental products; Dilatometry; Glass microstructure; Glass thermal properties; Opalescence; Opalescent glass; Phase separation in glasses; Scanning electron microscopy; SiO_2–Al_2O_3–K_2O; X-ray diffraction

1. Introduction

Research on and utilization of liquid–liquid phase separation have led to opalescence in glass gaining in importance. The mechanisms and the highly unexpected effects that lead to multiphase separation in glasses are the subject of numerous, comprehensive publications and monographs. Authors such as Bowen et al., [1], Vogel [2], and Kreidl and Uhlmann [3] must be mentioned in this connection. These fundamental studies on multiphase separation in glasses demonstrate that silicate glasses with fluoride additives [4,5], borosilicate glasses [6,7], and phosphosilicate glasses with different additives [8,9] are particularly suitable for producing glasses of high opalescence.

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[1] Dedicated to Professor Hiroshi Suga.

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In these systems, the high opalescence is based on liquid–liquid phase separation in glasses and on a controlled transition process of these simultaneous glass phases. In special cases, these multiphase glasses may even be designed to encourage crystal precipitation as could be shown for fluoride-doped glasses [10].

The objective in the development of all previous opal glasses for technical mass products (e.g. chinaware) and for specialized products used in the electronics industry was to achieve a relatively strong opal effect. By incident light these glasses appear almost opaque and white and by transmitted light, opaque and dark red. Keeping the application in mind, a technical process was developed in which, for reasons of economy, opalescence could be achieved immediately following cooling of the melted glass. The thermal expansion of these glasses is normally below 10×10^{-6} m/m K^{-1}.

Entirely new requirements must be fulfilled in the development of opalescent products for dental applications. For dental products, linear coefficients of thermal expansion of approx. $9.0–16.0 \times 10^{-6}$ m/m K^{-1} are required, according to the product, and the opalescence of the glasses must be similar to that of natural teeth. Furthermore, the glasses are processed in the form of glass grains or powdered glass. To ensure the correct optical qualities, the opal effect should remain almost unchanged, even after repeated heat treatment of the base glass.

2. Experimental

To achieve the properties required of opal glasses for dental applications, new glasses derived from the SiO_2–Al_2O_3–K_2O system were developed. In this study, glasses with a composition in the following range were analyzed with regard to their microstructure and their thermal properties: 48 to 66 wt% SiO_2, 5 to 20% Al_2O_3, 3 to 15% K_2O with additives of 3 to 12% Me(II)O, where Me(II) is Ca, Mg, Sr or Ba, as well as additives of 0.5 to 5% P_2O_5 and 3 to 12% Na_2O under the simultaneous influence of further additives, for example Li_2O, ZrO_2, TiO_2, and La_2O_3, up to 6 wt%.

In the experimental part, the glasses were melted between 1500 and 1600°C. Following appropriate homogenization through cooling, a glass frit was produced. The glass examined with regard to phase development and microstructure had a grain size of less than 90 μm. Opal glass in monolithic form was produced from these glass grains with subsequent heat treatment.

Microstructure development was examined using scanning electron microscopy (SEM; Carl Zeiss, DSM 962) and possible crystal phase development using X-ray diffraction (Siemens D500, Diffrakt. using Cu-K-alpha-radiation).

Thermal properties were determined with a dilatometer (Netsch, 402 TMA). For the dilatometric measurements, samples measuring 26 × 6.5 × 5 mm were produced. They were prepared in the following manner. Powdered glass smaller than 90 μm was thermally sintered under vacuum at temperatures of 940°C $min^{-1}$and 960°C m^{-1}. Subsequently, plane-parallelism of the reference surfaces for the measurement of length were achieved by grinding and polishing.

The test parameters for the dilatometer measurements were: heating rate, 5 K min^{-1}; atmosphere, still air.

The thermal properties of the dental opal glass were compared with those of conventional dental glass–ceramics.

3. Results

With the systematic variation of chemical synthesis in the composition range [11] mentioned in Section 2, special opal glasses for dental applications were developed that demonstrated the particular opal effect observed in natural teeth. These glasses were analyzed with regard to microstructure development and thermal properties.

3.1. Microstructure development

Following heat treatment to approx. 1020°Ch, glass grains of a glass with the above composition and a concentration of approx. 2.5 wt% CaO and 2.5 wt% P_2O_5 demonstrated the following characteristic microphase development. In the SEM in Fig. 1, the grain boundaries between the individual glass particles are closely sintered and there are almost no voids. Thus porosity is minimal. These signs indicate that the viscous flow process has begun. When vacuum is applied during the heat treatment, this process leads to the formation of a dense microstructure in the glass product.

Microphase separation within the glass matrix is important for achieving the desired optical properties, opalescence in particular, with simultaneous high transmission of

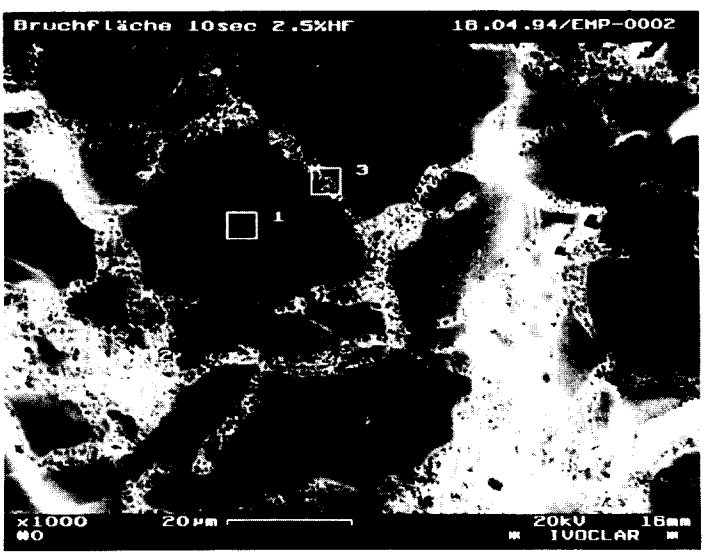

Fig. 1. Overview of the microstructure of opal glass for dental applications from the system SiO_2–Al_2O_3–K_2O containing 2.5 wt% P_2O_5.

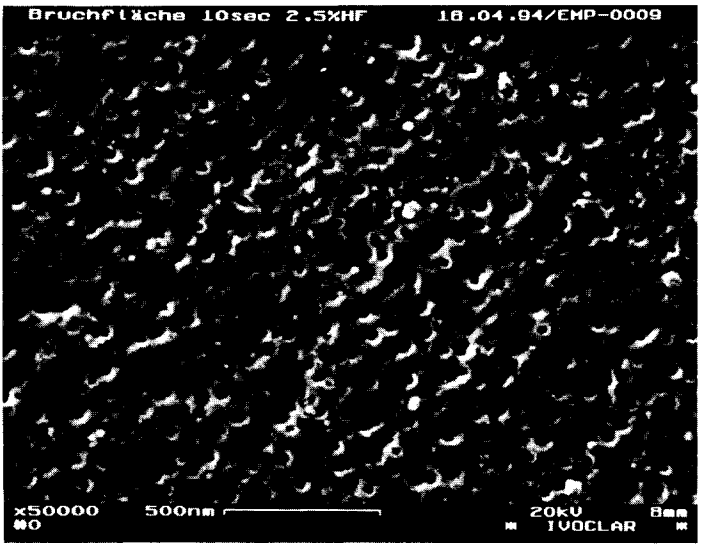

Fig. 2. Detail from Fig. 1 (area 1) showing the glass structure. It is quite clear that liquid–liquid phase separation is involved. Droplets measure less than 100 nm.

the glass sample. High-resolution SEM with 50000 × magnification (Fig. 2) was used to study the glass grains (Fig. 1).

By use of SEM, separation processes may be observed in which micro-droplet glass phases with a diameter of approx. 60–200 nm appear. As shown in Fig. 2, the number of these micro-droplet phases is relatively high. An optical property similar to the opalescence of natural teeth is achieved as a result of this phase separation.

As a result of systematic materials development, it can be assumed that this droplet glass phase contains phosphate and specific amounts of Me(II) oxides. This phase, however, is glassy, and the formation of the phosphate crystals could not be established by X-ray diffraction.

Microanalysis of the interface between the former surface of the glass grain and the interior of glass (Fig. 1) is of particular interest. The results of SEM (magnification 30000 ×) shown in Fig. 3 demonstrate that isolated crystallites are formed in this interface. X-ray diffraction analysis was also used to establish crystallite formation. Thus it was shown that the crystals measuring approx. 0.5–1 μm in Fig. 3 are leucite crystals of the type $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ [12]. These crystals, however, are also relatively small in comparison to other leucite-based glass-ceramics [13] and they are concentrated only in the interface areas depicted. Thus optical transmission is not significantly influenced.

Fig. 4 shows the very close contact area of the interface, containing the leucite crystals, and the glassy phases and the surrounding phase-separated glass structure.

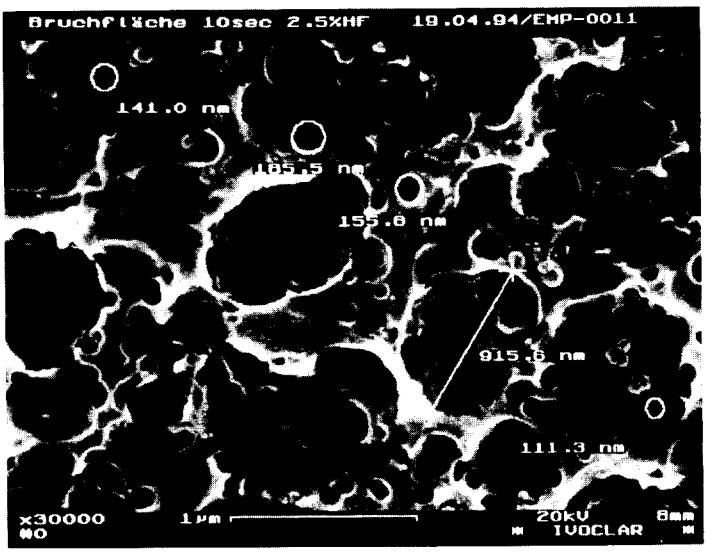

Fig. 3. Detail from Fig. 1 (area 2) showing the inner surface on which the crystallization of primary crystals of the leucite type begins. Leucite crystals measure approx. 1 µm.

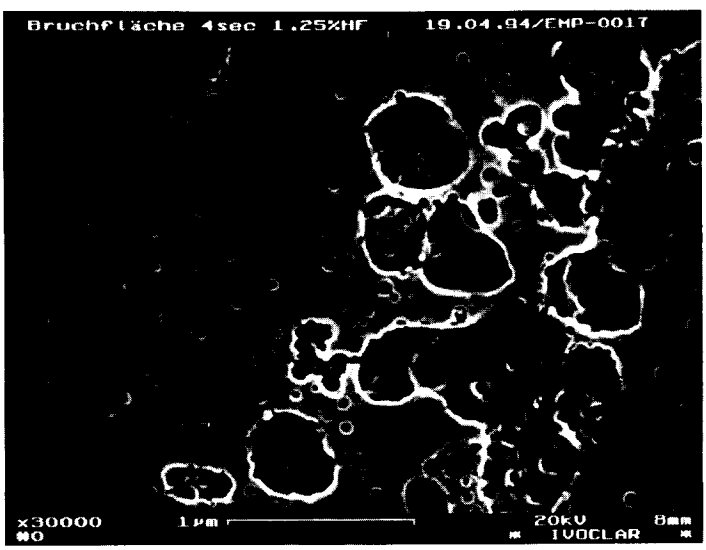

Fig. 4. Detail from Fig. 1 (area 3). The interface between the crystal area and the phase-separated glass area.

3.2. Thermal properties

The crystal phase formation illustrated in Fig. 3 together with the chemical composition of the base glass are, however, responsible for achieving very special properties. Thus linear thermal expansion of approx. 15.0×10^{-6} m/m K^{-1} can be achieved for a glass with a microstructure like that shown in Figs. 1–4.

Fig. 5 shows a typical (dL/L_0)–T curves as obtained for opal glasses used for dental applications. Figs. 6 and 7 show results from dental glass–ceramics in comparison with those from opal glasses.

Fig. 5 shows a typical dilatometer curve achieved for a dental opal glass with the microstructure shown in Fig. 1. According to this figure, the linear thermal expansion coefficient in the temperature range 100 to 500°C is 15.4×10^{-6} m/m K^{-1}. This coefficient of expansion serves as an indicative quantity for combining these opal glasses with other glasses and glass–ceramics used in dentistry. The fact that the materials (glasses and glass–ceramics) are built up in layers in later applications must be taken into consideration. As a result, the individual materials must be successfully coordinated with regard to their linear thermal expansion coefficients. Thus the compatibility of dental glasses and dental glass–ceramics was tested with the new opal glass for dental applications. Figs. 6 and 7 show dilatometric curves for two such dental glass or glass–ceramic materials. A linear thermal coefficient of expansion of 14.8×10^{-6} m/m K^{-1} (100–500°C) was established for dental glass–ceramic 1 (Fig. 6) and one of 15.8×10^{-6} m/m K^{-1} (100–500°C) for the glassy dental material 2 (Fig. 7).

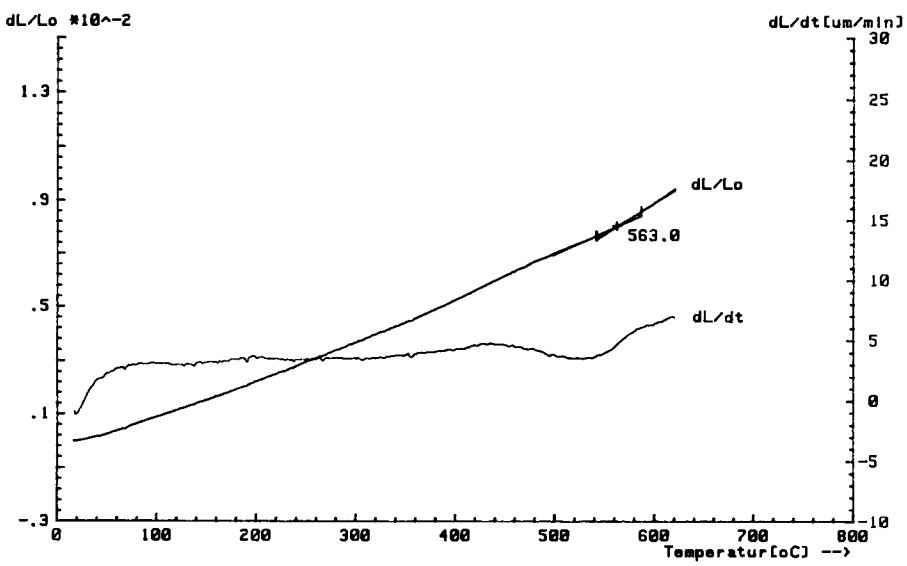

Fig. 5. Temperature-dependence of the change of length of dental opal glass. The linear coefficient of thermal expansion is 15.4×10^{-6} m/m K^{-1} (100–500°C). The T_g value is 563°C.

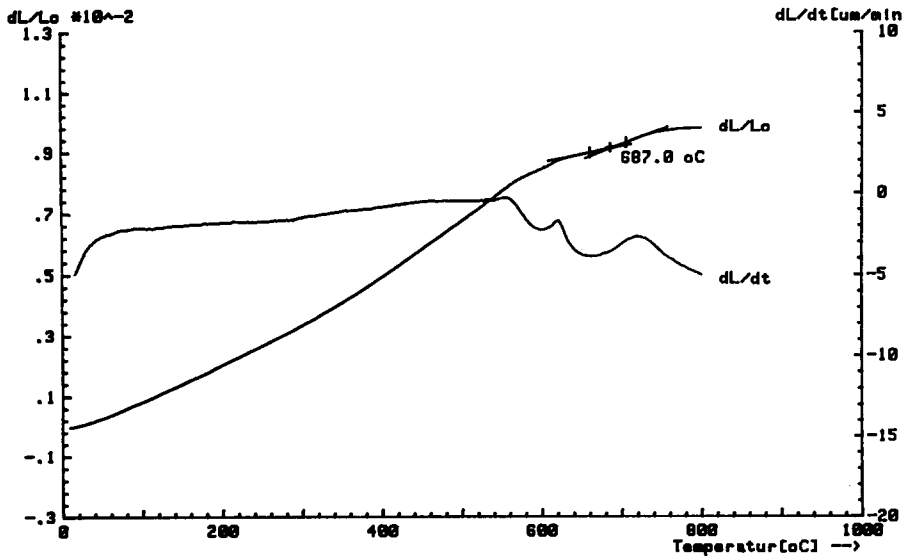

Fig. 6. Temperature-dependence of the change of length of a typical leucite glass–ceramic used as a dentine material. The linear coefficient of thermal expansion is 14.8×10^{-6} m/m K^{-1} (100–500°C). The T_g value is 687°C.

Both products are glass–ceramics. Dental material 1 is a leucite-based glass–ceramic. A special pressing procedure was used to form a dental all-ceramic product (e.g. dental crown) [14].

This glass-ceramic represents the basis of the synthetic teeth and is called dentine material. Other ceramics and glasses, e.g. dental material 2 and/or the opal glass were sintered onto the surface of dental material 1. Therefore the translucence of these substances must be similar to that of natural tooth surfaces. The glassy content of dental material 2, is, however, higher than that of material 1. The different microstructures of dental glass-ceramics 1 and 2 are also responsible for the differences between the curves shown in Figs. 6 and 7 and that shown in Fig. 5.

The curve in Fig. 7 is similar to those for conventional technical glasses. The same also applies to dental opal glass (Fig. 5). Thus an almost linear increase in the coefficient of expansion is registered up to the transformation range. The special nucleation and crystallization processes only begin above the transformation range. Glass–ceramic 1 (Fig. 6), however, contains a high crystal concentration. Thus comparison of the curve (dL/dt) in Fig. 6 with those in Figs. 5 and 7, reveals the discontinuity before the transformation range. In examining these processes, it must be noted that above the transformation range the nucleation and crystallization processes are responsible for the characteristic changes, as for other glass–ceramics. Below the transformation range, however, structural changes may occur that have not yet been fully clarified. Thus the sintering and reordering processes involved and the thermal properties of the crystal phases formed must be further examined.

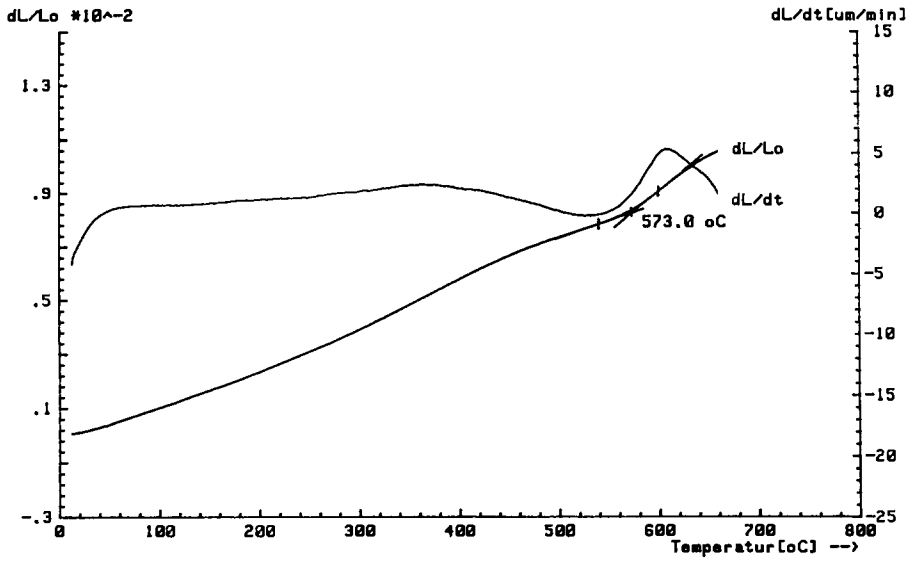

Fig. 7. Temperature-dependence of the change of length of a typical leucite glass–ceramic used as a dental transparent substance. The linear coefficient of thermal expansion is 15.8×10^{-6} m/m K^{-1} (100–500 °C). The T_g value is 573 °C.

Furthermore, from the curves analyzed in Fig. 5, it can be assumed that the dilatometrically established transformation range of the glasses is at approx. 550–570 °C.

As a result of these characteristic thermal properties of the glasses, a sintering process can be carried out to fabricate a monolithic dental product with the above optical properties at temperatures ranging between 920 and 1020 °C for 1 hour. Moreover, the main optical properties remain constant during short-term heat treatment of the glasses in the same temperature range.

4. Conclusion

It is possible to develop glasses derived from the system SiO_2–Al_2O_3–K_2O that can be used specifically for dental applications. SEM analyses provide the most important information for characterizing phase development. It is also evident that two mechanisms must be controlled simultaneously: (a) phase separation in the glass and (b) minimum surface crystallization at glass grain boundaries within the monolithic sample. Thermal examination of the relationship between (dL/L_0) and T establish the special thermal properties of opal glass for dental applications — a linear thermal expansion coefficient of approx. 15.0×10^{-6} m/m K^{-1}. Quantitative measurement of the optical properties of the dental opal glass is in preparation [15].

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