Thermal expansion and length stability of Zerodur in dependence on temperature and time

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The lengths and the thermal expansion values of the glass ceramic Zerodur show a reversible dependence on the thermal history within two temperature intervals. Typical effects associated with this dependence are, for example, isothermal length changes within and permanent length changes below the temperature intervals. It is assumed that relaxation causes the observed effects. The phenomena in the upper temperature range from 130°C to 300°C are related to the MgO content. The reversibility of the relaxation effects allows adjustment for lengths and thermal expansion values by appropriate cooling processes.

I. Introduction

Zerodur, a homogeneous glass ceramic, has an especially small thermal expansion, as shown in Fig. 1. In addition to the main field of application, which classically has been mirror substrates, new technical uses have become important, for example, laser gyros. For this application mechanical stability and the highest possible consistency of shape and length are required. In this case Zerodur is subjected to additional manufacturing processes such as vacuum bake out or coating processes and it is temporarily exposed to temperatures in the 300–500°C range. Although no irreversible property changes take place within this temperature range, subsequent cooling processes or temperature cycling at lower temperatures may slightly influence its characteristics.

This sensitivity was observed by Bennett[1] during a thermal expansion test between 20 and 300°C. In a first temperature cycling a deviation in the measured length change was observed between heating and cooling. In subsequent temperature cycles with the same sample and with the same rate, no further deviations up or down were observed. Similar results are reported by Gorski,[2] who observed a variation in the thermally induced length change for temperatures <250°C. Both authors observed permanent length increases at room temperature up to $\Delta l/l = 8 \times 10^{-6}$.

Jacobs *et al.*[3] observed two effects during a first temperature cycle between 27 and 207°C: a permanent length decrease $\Delta l/l$ of $\sim 2 \times 10^{-6}$ and nonequilibrium effects between 130 and 207°C, caused by the noncontinuous temperature variation in their measurement procedure. By recycling in the same temperature range no permanent length change occurs; however, the nonequilibrium effects are still found. Similar observations were made in a second temperature range from −80 to +27°C.

Shaffer and Bennett[4] report on quenching experiments in which plane mirrors of Zerodur were quenched in air and through contact with cold metal supports. The temperature range was 50–300°C. A permanent deformation was observed, in particular, for quenching temperatures >200°C.

All the previously discussed measurements and observations can be related to in-house experimental results on Zerodur. The following reports on these findings.

II. Background

The observed dependence of thermally induced length changes of Zerodur on thermal history points to the structural relaxation process as the cause. Such relaxation processes are well known in glass. They are of fundamental importance for glass formation and the stabilization of glass properties in the transformation range and, therefore, have been studied extensively.[5]

Less known is that the cooling rate dependence as well as the isothermal changes of the glass properties are observable even near room temperature. This is, for example, of technical importance for thermometers made from glass.[6]

The dominant dependence of this low temperature relaxation on the type and combination of alkali ions present in the glass leads to a model concept, where the

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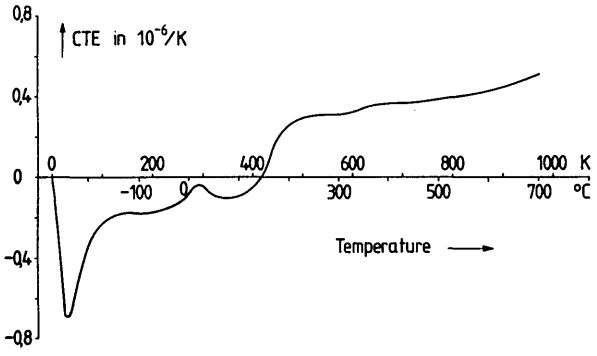

Fig. 1. Coefficient of thermal expansion (CTE) of Zerodur between 0 and 1000 K.

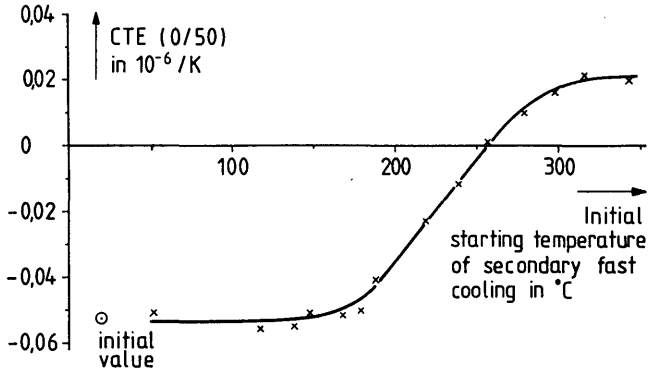

Fig. 2. Variation of the coefficient of thermal expansion CTE (0 to +50°C) of Zerodur—primary annealing at 0.1 K/min—as a function of the initial temperature of a secondary cooling in open air to room temperature.

observed effects are due to the rearrangement of such ions or ion groups within the glass structure with appropriate time requirements.[7]

The glass ceramic Zerodur contains a glass and a crystal phase, the latter consisting of high quartz solid solution crystals.

It is known that structural rearrangement processes are also important in these crystals. Thus the order–disorder phase transition in β-eucryptite, $Li_2O \cdot Al_2O \cdot 2\,SiO_2$, which is a special variant within the family of high quartz solid solution crystals, has been repeatedly studied at ~480°C (see, for example, Ref. 8). For $MgO \cdot Al_2O_3 \cdot 3\,SiO_2$, structural rearrangements were observed in the temperature range from 800 to 1000°C,[9] where unordered crystals order themselves at a holding temperature of 850°C, and, conversely, ordered crystals exhibit a change toward disorder at a holding temperature of 1000°C. Finally, Roye[10] demonstrated that the lattice parameters of $0.6\,MgO \cdot 0.4\,Li_2O \cdot Al_2O_3 \cdot 2\,SiO_2$ depend on the temperature history. By measuring the lattice parameters during a temperature cycle from room temperature to 580°C and back to room temperature, the c-lattice constant measures constantly smaller in value on heating up rather than on cooling down.

These results point out that one must reckon with relaxation effects in high quartz solid solution crystal-containing glass ceramics in the glass phase as well as in the crystal phase. One or the other relaxation effect may be avoided through an appropriate chemical composition change, whereas other relaxation effects cannot be circumvented without affecting the important characteristics of the glass ceramic.

III. Experimental Procedures

The measurements of the length change of Zerodur test samples described in this paper were carried out in a push rod dilatometer, made of titanium silicate (ULE 7971). The push rod motion can yield a 5-nm sensitivity using an inductive coil (LVDT). Thus, the relative length change of a 100-mm long test sample can be determined to a $\Delta l/l = 5 \times 10^{-8}$. To calibrate the coil a laser interferometer (HP 5526A) was used. The calibration of the titanium silicate system was performed using samples measured by S. F. Jacobs (University of Arizona) as well as by W. Gorski (PTB Braunschweig).

To investigate the influence of the chemical composition on the relaxation effects, experimental melts using standard methods were carried out. The batch was melted in ½ liter quartz crucibles at ~1620°C and homogenized in platinum crucibles at ~1580°C. Then the glass was poured into a block mold of ~12 × 7 × 1 cm. After annealing the glass samples the ceramization was carried out by a two-step process. The first temperature treatment at 730°C for 2 h mainly provides for the formation of nucleation sites. The glass is subsequently held at 850°C for 2 h allowing crystal growth to take place.

IV. Measurement Results

A. Temperature Range from 130 to 320°C

To determine the location and limits of the temperature regions within which a dependency of the properties on the cooling rate can be expected, fifteen dilatometer samples were quenched from temperatures between 50 and 350°C in free room air and then the CTE (0/50) was measured. The samples were made from a piece of Zerodur which had been initially annealed at 0.1 K/min to room temperature.

The results shown in Fig. 2 indicate that deviations of the CTE value from the initial -0.052×10^{-6}/K do not begin until ~130°C, if one considers that the reproducibility error is 5×10^{-9}/K. The CTE values increase at higher temperatures until a saturation value of $+0.02 \times 10^{-6}$/K is reached at ~320°C. A significantly different CTE value from the aforementioned one is not obtained even after quenching from 400 and 450°C.

Analogous with the general behavior of multicomponent silicate glasses, the CTE exhibits to a large extent linear dependence on the logarithm of the cooling rate R when cooling starts from the same temperature (Fig. 3). The change Δ(CTE 0/50) caused by a change ΔR of the cooling rate (starting from 320°C) can be formulated for Zerodur as follows:

$$\Delta(\text{CTE } 0/50) = 2.5 \times 10^{-8} \log_{10}\left(\frac{\Delta R}{\text{K/min}}\right).$$

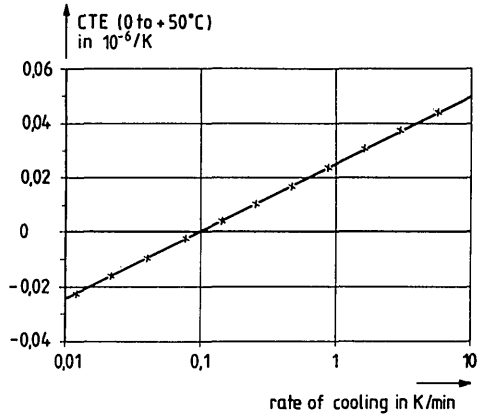

Fig. 3. Variation of the coefficient of thermal expansion CTE (0/50°C) as a function of the cooling rate from 320°C to room temperature, normalized to a cooling rate of 0.1 K/min.

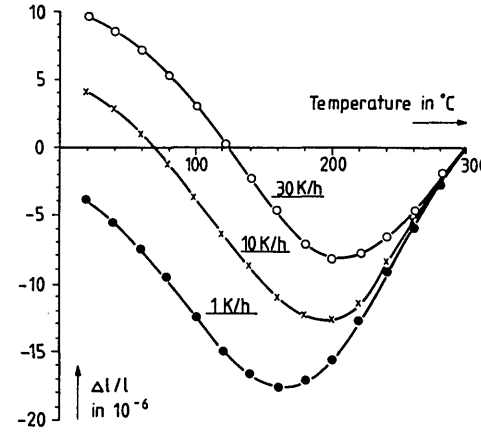

Fig. 4. Thermal length contraction of Zerodur for three cooling rates from 300 to 20°C.

As a consequence of the change in cooling rate from 320°C, not only the CTE (0/50) value—which is used as an indicator—changes in the range between 130 and 320°C but also the total contraction course and with it the sample length at room temperature (Fig. 4). To characterize this dependence of the length l_{20} at room temperature on the cooling rate R, we use in the following the length difference $\Delta l_{20}(R)$ which results from an arbitrary rate R compared with our normal rate of $R = 0.1$ K/min. The relative value $(\Delta l/l)_{20}$ of this length difference will be referred to in the following as rate-dependent length difference (RDLD).

Independent of the foregoing thermal history the length at room temperature and the CTE prove to be stable within changes of $\Delta l/l > 5 \times 10^{-7}$ and CTE (0/50) $> 1 \times 10^{-8}$/K, respectively. The time stability of the length at a given temperature decreases with the approach and entry into the critical temperature interval of 130–320°C, whereby the change in length depends on the foregoing cooling rate. Thus, fast reheating to a given temperature after previous fine annealing results in an isothermal dilatation whereas an isothermal contraction is observed if the previous cooling took place relatively rapidly; this is demonstrated in Fig. 5 for two representative cooling rates.

The influence of different batch components on the relaxation behavior of Zerodur was investigated in a series of test melts. Evaluation of these tests shows that the previously described dependence of length on the cooling rate is largely effected by the MgO content. Figure 6 demonstrates this influence on the RDLD value: a 2.3 wt. % MgO-containing glass ceramic has a RDLD of 3×10^{-5} while the value diminishes to near zero with decreasing MgO content.

B. Temperature Region from −70 to 40°C

Relaxation effects similar to those described in the last section are observed in the temperature range from −70 to 40°C. The effect of this relaxation is represented in Fig. 7 where the length change due to thermal cycling at 1.25 K/min between −60 and 100°C is shown. A similar cycle, however, with isothermal 1-h holdings

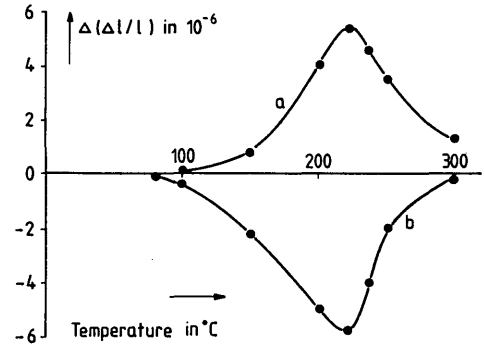

Fig. 5. Isothermal change of length of Zerodur at temperatures between 100 and 300°C. Length change $\Delta(\Delta l/l)$ after 90-min holding at any given temperature: *a*, after previous cooling from 400 to 20°C with a rate of 1.5 K/h; *b*, after previous thermal shock from 400 to 20°C in free air (4-mm diam rod). Approximately 20 min were needed for heating from room temperature and thermal equilibration.

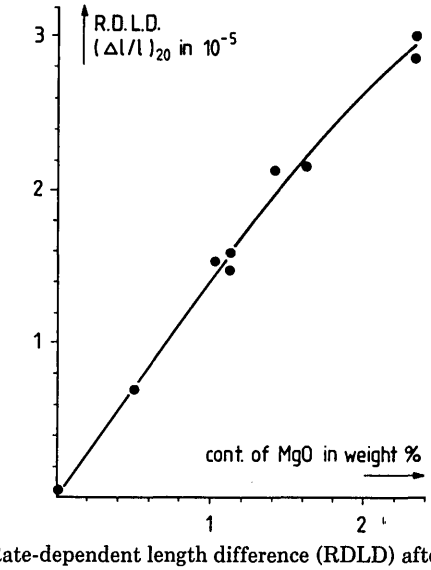

Fig. 6. Rate-dependent length difference (RDLD) after rates of 6 K/h and fast cooling in free air from 300°C of different glass ceramics as a function of the MgO content.

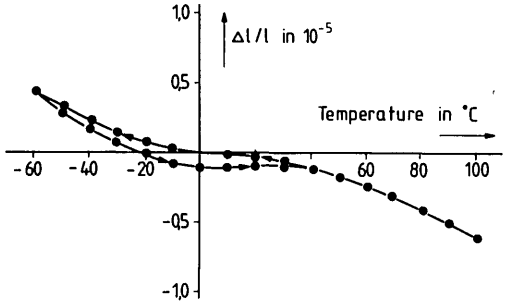

Fig. 7. Hysteresis in the course of relative length change $\Delta l/l$ during a thermal cycling process of Zerodur; temperature rate = 1.25 K/min.

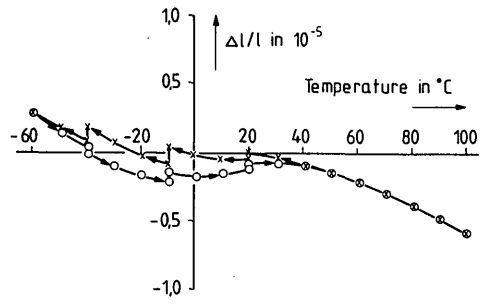

Fig. 8. Hystersis in the course of relative length change $\Delta l/l$ during a thermal cycling process of Zerodur (temperature rate = 1.25 K/min) with isothermal one-h holdings at 20, −10, and −40°C in cooling and heating, starting temperature +100°C.

at 20, −10, and −40°C is shown in Fig. 8. By holding isothermally, the state of structural equilibrium is approached and the opening of the bow at −10 and +20°C decreases to $\sim\Delta l/l = 0.5 \times 10^{-6}$. Almost complete isothermal equilibrium is reached after ~24 h whereby the rate of the temperature change naturally affects the occurring length change (Fig. 9).

A freeze of this relaxation, which we consider to take place when no measurable length change occurs within 100 h, can be expected at temperatures below −90°C. Therefore, in the main region of use (−50–100°C), permanent length changes due to temperature changes are not anticipated.

V. Discussion of the Results

Structural relaxation in Zerodur within two temperature regions (−70 to +40°C and 130 to 320°C) leads to rate-dependent lengths. In heating processes the departure from the equilibrium temporarily results in a length smaller than the equilibrium length, whereas during cooling processes the departure from equilibrium temporarily results in a length larger than the equilibrium length. Within these temperature regions the equilibrium is mainly restored within 2–24 h.

With decreasing temperature below either of these regions structural configurations are progressively frozen, so that permanent properties are attained. On the other hand nonequilibrium configurations become increasingly important with the approach of the critical temperature regions, which can cause, for example, isothermal length changes. The extent of thermal relaxation effects increases with increasing rates of temperature change. The values of RDLD usually lie between 1×10^{-6} and 1×10^{-5}.

The advice given in Ref. 11 that prefabricated pieces of Zerodur which are to be used as high precision optical elements should not be heated to temperatures above 150°C follows directly from the results discussed in Sec. IV.A. The threshold temperature of 150°C generally does not limit the applications of Zerodur; however, it indicates the lower limit of a temperature interval in which secondary thermal effects require attention with respect to the cooling rate. To obtain high precision optical elements the results shown in Fig. 3 can be used to determine the tolerances, within which the cooling rate has to be reproduced. If, for example, the change

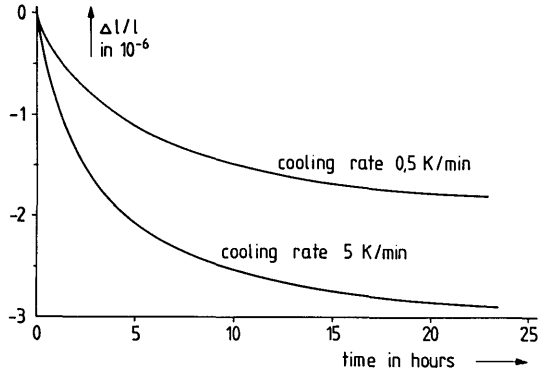

Fig. 9. Isothermal change of relative length of Zerodur at −30°C after cooling from +100°C to the said temperature at 0.5 and 5 K/min.

in CTE (0/50) between two heating processes is to be held below 0.1×10^{-7}, the appropriate cooling rates must not differ by more than a factor of 2.5. The unrestricted reversibility of the structural equilibrium adjustment permits intermediate thermal treatments with any time program without influence on the characteristic values, which are exclusively determined by the final annealing.

In conformity with the above statements, the results in Refs. 1 and 2 as well as part of the results in Ref. 3 can be explained. The permanent length reduction of ~2 $\times 10^{-6}$ at room temperature after a first temperature cycle from 27 to 207°C and back again to 27°C, which was found in Ref. 3, can easily be explained on the basis of our results in that the previous cooling rate from temperatures ≥207°C was effectively higher than the one described in the test; the suggestion given in Ref. 3 that the length difference is due to internal stresses is in our opinion not very likely.

Furthermore we consider it unclear that the instability ("failure of return"), postulated in Ref. 3 to be permanent after a waiting time of 29-h maximum, represents a real permanent state. Based on the knowledge with glass thermometers, in which the secondary effects are of the same order of magnitude,[12] the time spans for relaxation "remnants" can be of the order of 100 h for $\Delta l/l$ changes of $\sim 1 \times 10^{-6}$.

As a logical consequence of the previously described material properties, the deformation of the Zerodur mirror described in Ref. 4 may be due to quenching from a temperature >150°C. If during the film coating operation, mentioned in Ref. 4, a uniform temperature throughout the mirror cannot be achieved, it is still possible to reverse the distortion that occurred during coating by a subsequent heat treatment.

The observed dependence of the thermal relaxation effects in the temperature range from 130 to 320°C can be continuously decreased by decreasing the MgO content pointing to the MgO content as the cause of the relaxation. So, a glass ceramic free from the relaxation effect in the temperature interval from 130 to 320°C must not contain MgO; however, the development of such a glass ceramic is not so simple as stated, because the influence of the MgO has to be considered; for example, the MgO has a beneficial effect on the viscosity at the melting temperature as well as on the characteristic of the thermal length change.

Nevertheless, a modified glass ceramic with almost identical properties to those of Zerodur but without the relaxation effect in the temperature interval from 130 to 320°C has been developed and is now being tested.

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OF INTEREST

At a recent meeting of The American Physical Society, astrophysicist David Schramm of the University of Chicago reviewed a list of reasons for believing that there's a lot of matter out there that is not shining. In fact, it may be that the bulk of the matter in the universe is not shining, either because it is not hot enough to emit radiation that we can see or because it consists of particles that seldom interact with ordinary matter. Astronomers refer to this stuff as "dark matter."

There is strong evidence to support this idea. For example, the observed movement of galaxies is such that scientists believe more matter exerts a gravitational attraction than can be seen; dark matter may cluster around galaxies and their surrounding area; or it may be distributed more evenly throughout the cosmos.

Dr. Schramm, referring to this missing matter, says, "It's really the light that's missing. The matter seems to really be there as far as how it interacts gravitationally."

Some theories indicate that there might be two or more kinds of dark matter, each distributed in a different manner. One kind would center around galaxies, while others might be thinly dispersed throughout space. The amount of dark matter determines whether our universe ultimately collapses or expands forever.

It appears that matter is at a critical density -- just at the crossover point. A critical density universe is a universe that is right at the boundary between a universe that will fall in, eventually back to a very high density state -- the big crunch -- and a universe that will continue to expand forever and keep cooling into what Schramm calls "the big chill."

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