

The double-beam optical dilatometer is the ideal instrument to determine the temperature at which a ceramic body achieves full vitrification, with no bloating, in a minimum length of time.

Using the **Optical** Dilatometer

TO DETERMINE
SINTERING
BEHAVIOR

Traditionally sintered ceramic bodies, such as stone-ware or porcelain-ware, undergo a viscous flow sintering process. The driving force is mainly given by the surface tension of the liquid glassy phase, and the speed of the process is controlled by the viscosity of the glassy phase.

During the past few decades, the concept of fast firing has gained more and more acceptance in the industry. This has led to the need for development of fast-sintering ceramic bodies that can yield a fully vitrified ware with a total firing cycle of <1 h.

The most important factor to increase the sintering speed in a viscous flow sintering process is to decrease the viscosity and to increase the surface tension of the glassy phase. There are several drawbacks in decreasing the glassy phase viscosity, including deformation in the ware because of the loss of strength during the firing, and bloating of the ware because of bubble growth inside the body.

Both of these problems are strictly related to the low viscosity of the bonding glassy phase at high temperature. The deformation occurs when the body itself cannot withstand its own weight. The bloating occurs when the viscosity of the glassy phase becomes low enough to enable the fast growth of residual gases bubbles, which remain present in the body.

A major concern in the design of fast-sintering bodies is the determination of the best top firing temperature, which is the temperature at which the given body composition is able to achieve full vitrification, with no bloating, in the minimum time. This is not a trivial problem to approach, because it implies the ability to follow the sintering process without introducing perturbation.

The new double-beam optical dilatometer is the ideal instrument for this task. It can follow, with dilatometric resolution, the sintering of the material with no contact, directly during a fast-firing cycle.

Test Procedure

The double-beam optical dilatometer (Model MISURA, Expert System Solutions) is designed to reach a high heating rate to reproduce industrial firing cycles. It uses a second optical path

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as reference beam to correct the mechanical drift of the sample holder. The first optical path is used to measure the top of the sample, while the second optical path is focused on the sample holder. Any drift is instantly corrected from the actual measurement.

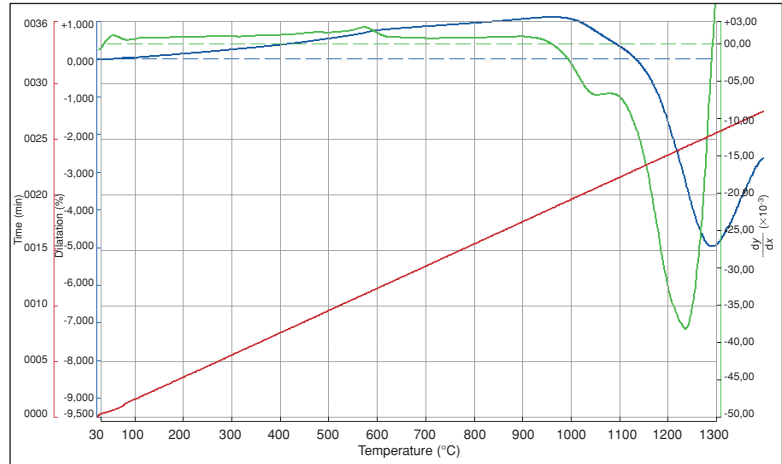
This innovative design provides an important feature for this instrument. There is no need for a calibration curve, and, thus, it is possible to change the heating rate or to design a complex heating curve. The measurements are absolute, because they are not affected by the sample holder or by a push rod, as in traditional dilatometers.

Unlike electronic dilatometers, the resolution of an optical dilatometer cannot be less than $0.1 \mu\text{m}$, because it is limited by the wavelength of the light. The optical dilatometer can give reproducible results with a resolution of $1 \mu\text{m}$, over a sample length of 15 mm , which is 1 part over 15000. This resolution may be considered too low, but it becomes valuable for a sintering process where the size variation may reach several percentage points.

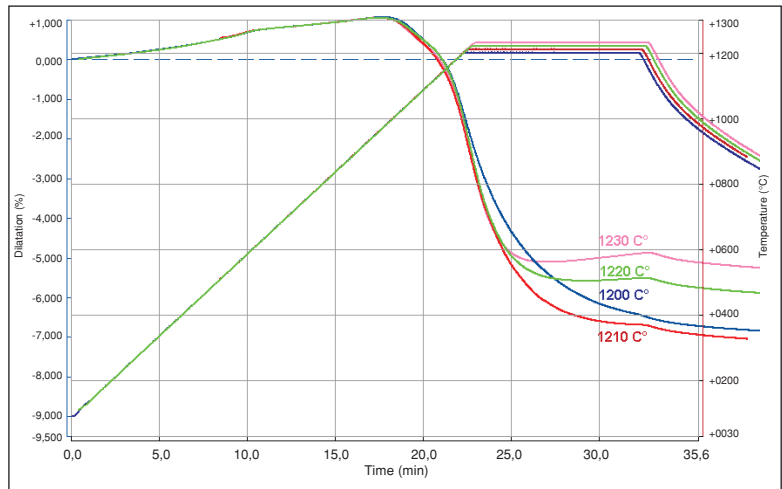
The first optical path is driven by a step motor to keep it always aligned with the top of the sample. This design concept allows measurements to be conducted with the same resolution over the full size of the sample; i.e., the measurement never is out of scale. This feature enables perfect following of a viscous flow sintering process, yielding the true sintering curve in real time.

The sample is prepared using a laboratory press equipped with a steel die that yields a sample $15 \times 5 \times 5 \text{ mm}$. The powder can be prepared according to any standard laboratory procedure or it can be taken directly from the production line. Maximum care must be taken in the preparation of the sample, because the measurement is largely affected by powder preparation, humidity and specific pressure.

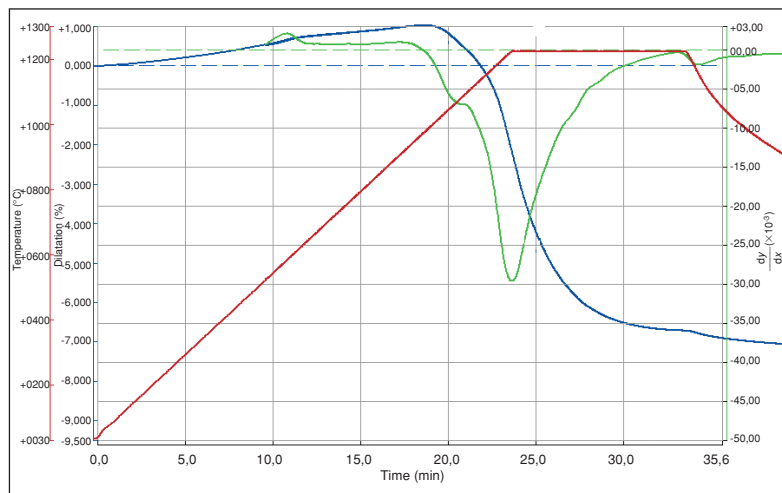
Normally, the samples are pressed under a specific pressure of 400 or



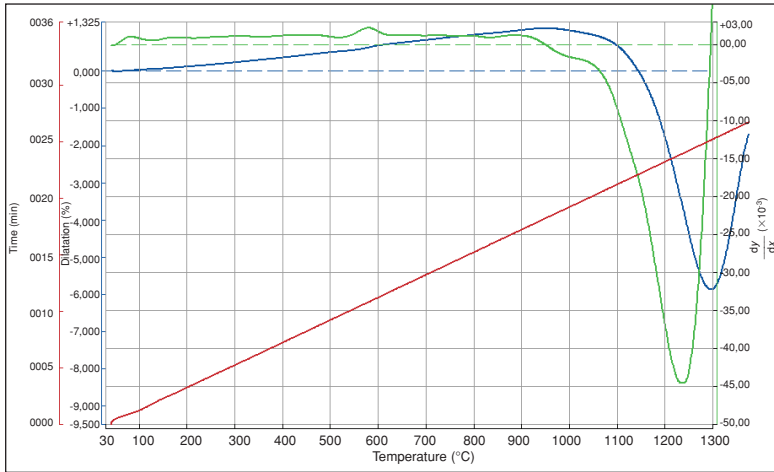
Fast-firing porcelain body A shows maximum sintering rate at 1230°C .



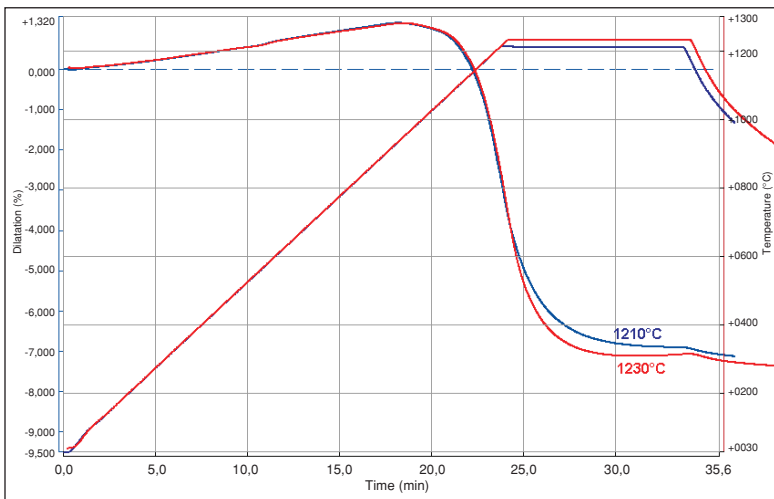
Body A with various dwell temperatures: small temperature change affects the sintering too much. At 1210°C for 10 min, the body reaches a stable dimension with no bloating.



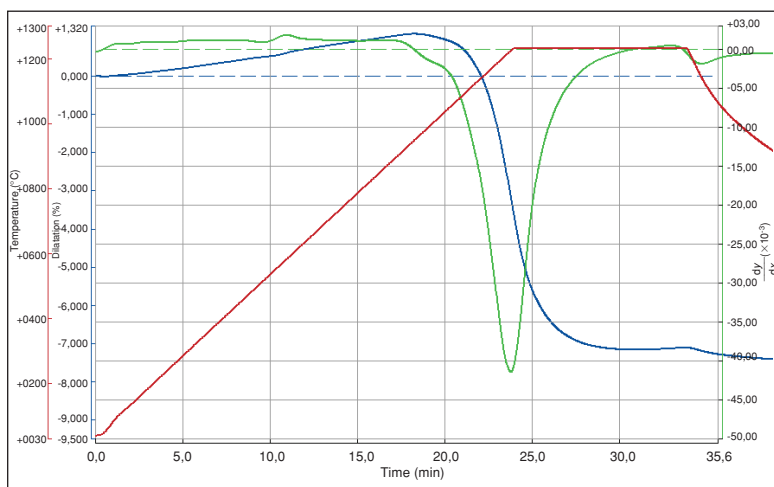
At the optimum firing temperature of 1210°C , the derivative curve of sintering (green) reaches the zero line after 10 min of dwell.



Fast-firing porcelain body B shows maximum sintering rate at 1230°C.



Body B with various dwell temperatures. Temperature difference of 20°C has little effect on sintering. Optimum top firing temperature is 1230°C.



At the optimum top firing temperature of 1230°C, the derivative curve of the sintering (green) reaches the zero line after 6 min of dwell, and the size remains stable.

500 kg/cm², according to the normal industrial practice. However, the samples can be cast or cut from an industrially prepared ware. The sintering tests described later are of samples that have been wet milled and dry pressed with 5% humidity at 400 kg/cm². Because the samples undergo a fast-heating cycle, they must be completely dry, otherwise they may explode inside the dilatometer furnace.

The tests are conducted using a heating rate of 50°C/min, according to various temperature profiles. The first test is always conducted using a continuous heating ramp up to 1400°C so as to identify the sintering and bloating attitude of the sample.

The temperature interval where the sintering speed reaches the maximum can be identified by plotting the derivative of the sintering curve. This corresponds to the negative peak of the derivative curve of the sintering.

After this test, a series of firing profiles is designed, with a dwell time at temperature of 10 min in the maximum sintering speed range.

For example, if the maximum sintering speed at 50°C/min is found to be 1200°C, then tests are conducted with 10 min dwell times at 1190, 1200 and 1210°C to identify the best firing profile. The best temperature is found when the maximum shrinkage is reached and there is no further shrinkage or bloating. If the dwell temperature is too high, after the sintering has occurred, the size of the sample is not be stable, but it begins to increase again, showing a tendency to bloat.

The concept that decreasing the firing cycle is necessary to increase the top firing temperature is directly related to the Arrhenius law. This law states that, after the activation energy is reached, the viscosity of the glassy phase decreases with a logarithmic law as the temperature increases. Decreasing the viscosity of the glassy phase too much (i.e., increasing the temperature too much) results in a sample that is not

able to withstand its own weight or that may begin bloating. The sintering curves conducted at various dwell temperatures enable precise identification of the best firing profile for any given body composition.

A Fast Firing Porcelain Body

This study has been conducted to compare the sintering behavior of various ceramic bodies designed for fast firing.

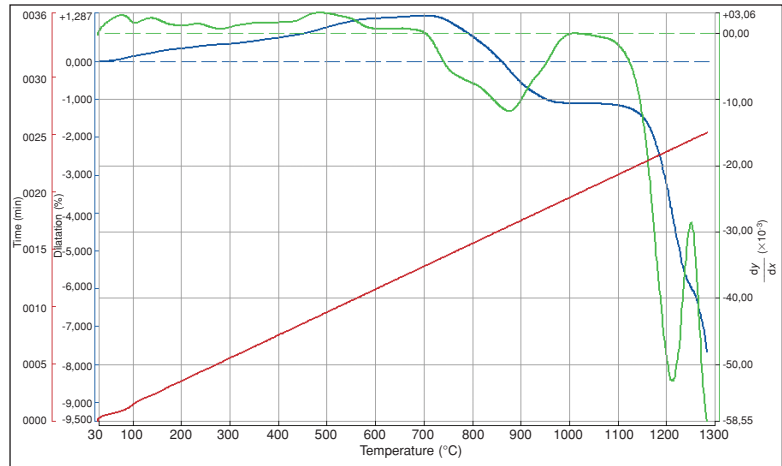
Traditional porcelain bodies are usually made of natural raw materials, typically kaolin, feldspar and quartz. However, in recent years, these compositions have been completely redesigned to decrease the firing temperature and the total firing cycle.

A first step has been to decrease the use of kaolin, substituting it with more-plastic and more-fusible kaolinitic or illitic clays. The second step has been the introduction of ready-made glassy phases, which may interact with the other raw materials of the body, resulting in a much faster sintering behavior. The use of glass-ceramic frits provides increased strength and body whiteness, solving the problem of decreased mechanical properties caused by the use of simple glass as a flux.

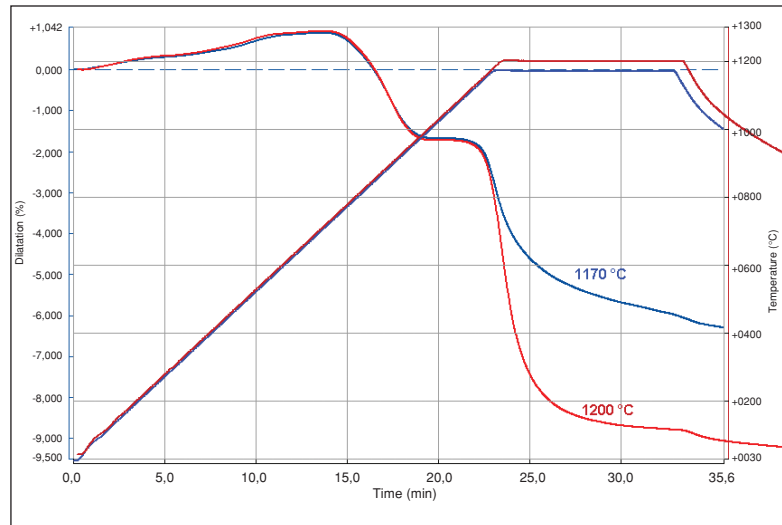
Four sets of tests have been conducted using ceramic bodies designed for faster firing cycles. The first and the second sets use a ceramic body made of natural raw materials and the third and the fourth sets use a new ceramic body having a high percentage of glass-ceramic frit.

Three graphs are prepared for each material:

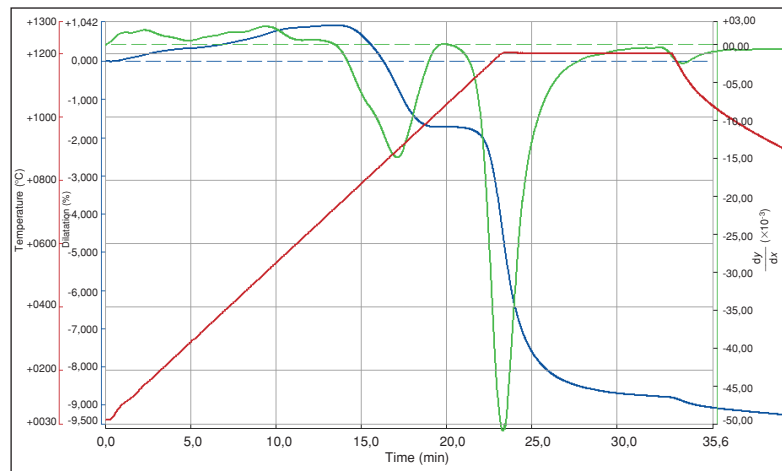
- The first graph is plotted with sintering percentage as the y-axis and temperature (in degrees celsius) as the x-axis. The test is conducted using a continuous heating rate up to 1400°C. The derivative curve of the sintering also is plotted to identify the maximum sintering speed.
- The second graph is plotted with time on the x-axis and temperature in the secondary y-axis. This graph



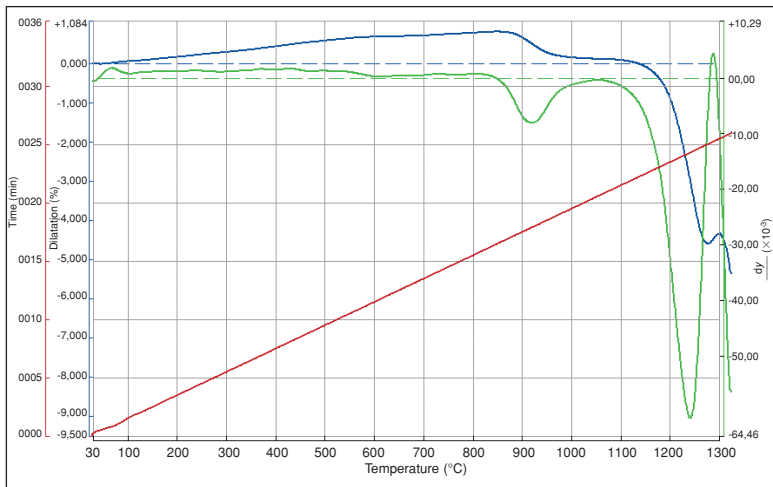
Fast-firing porcelain body with addition of a glass-ceramic frit. Maximum sintering rate is slightly above 1200°C (negative peak in the green curve).



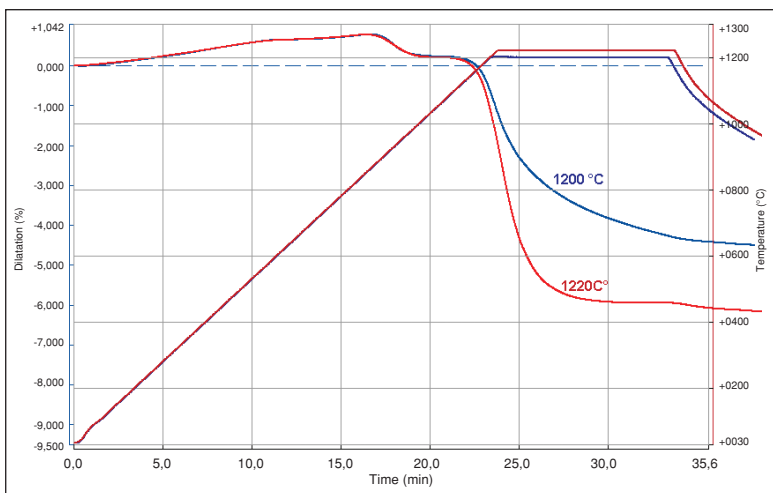
Optimum top firing temperature is 1200°C, at which the body reaches a shrinkage >9%.



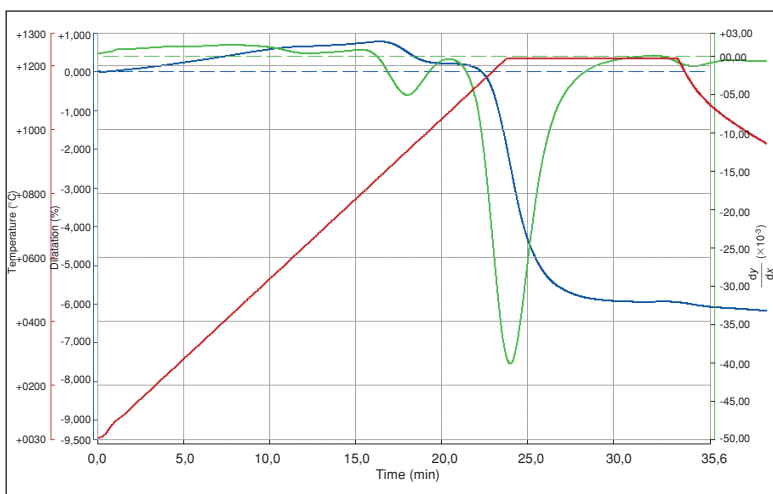
At the optimum top firing temperature, this body shows the highest sintering speed, and the shrinkage stops after 5 min of dwell.



Fast-firing porcelain body with addition of last generation of glass-ceramic frit. Maximum sintering speed is at 1230°C.



Optimum top firing temperature is 1220°C, with shrinkage <7%.



At the optimum firing temperature, the shrinkage stops after 6 min and there is no bloating.

clearly identifies the firing curve. All of the firing tests are plotted on this graph. Each one is identified using the same color in the sintering curve and in the temperature curve.

- The third graph represents the best firing curve of the previous plot, with the derivative against the time of the sintering curve. The temperature scale is on the left y-axis and the derivative is on the right y-axis. This curve shows that, when complete sintering is achieved, the sintering speed derivative reaches the zero point and remains there during the rest of the temperature dwell.

Comparison of the four materials shows that the first composition has a low sintering speed and a narrow sintering range, because, for a small temperature increment, the sintering decreases and the bloating begins.

The second composition is better, because it shows a small, progressive increase of sintering with the temperature increase, and it reaches a point where it remains stable over the entire dwell temperature interval.

The third composition shows a remarkably high sintering speed; however, it can reach a stable dimension in a short time, remaining stable over the entire dwell temperature interval. This composition reaches a high shrinkage in a short time, with a sintering speed that is much higher than the previous tests.

The fourth composition shows a behavior similar to the previous composition, but with much less total shrinkage. This composition reaches a stable condition of full sintering after few minutes at 1220°C; however, the total shrinkage is <7%.

Sintering Test Results

The results of the sintering tests can be correlated with other laboratory tests, such as chemical analysis and mineralogical analysis, to achieve a complete understanding of the process. The sintering speed is highly affected by all the physical, chemical and technological parameters. The full comprehension of the dynamics of the process is necessary

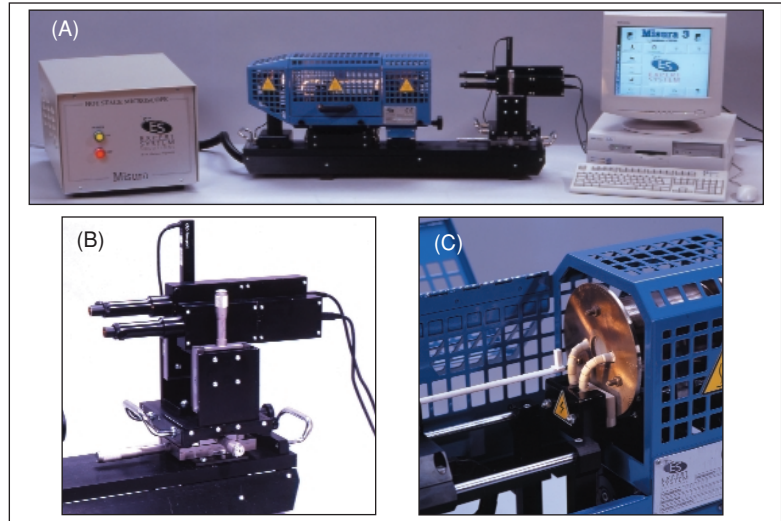
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to learn how to control the sintering step when it becomes faster.

The tests using the glass-ceramic materials are of particular significance, because the sintering speed is strongly affected by the devitrification process. The two examples shown here represent two extremes: in the first sample, the addition of a glass-ceramic material yields a much higher shrinkage compared with a traditional body, and, in the second sample, the opposite occurs.

These extremes occur because of a particular design of the glass-ceramic phase that interacts with the matrix and yields a crystalline phase that has a lower density compared with the starting glass. The decrease in density implies an increase in volume, and the macroscopic effect is a decrease in shrinkage.

In the third example, the glassy phase is simply devitrified stoichiometrically, yielding a crystalline material of the same composition as



(A) Optical dilatometer components. (B) Double-beam measuring device of optical dilatometer. (C) Sample holder of optical dilatometer.

the glass. In this case, the specific volume of the crystal is normally lower compared with that of the glass (i.e., specific gravity of quartz is 2.65 and specific gravity of quartz glass is 2.2). This type of glass-ceramic material added to a ceramic body always produces an increase in shrinkage. ■