

# Sintering Behavior of Glass-Ceramic Frits

*Combining DTA and HEMA data may provide a simple and quick method for describing the sintering/crystallization process for different glass compositions.*

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**G**lass-ceramic materials are generally obtained through the controlled crystallization of glass. A gradual decrease in transparency is the most obvious indicator of a transformation in the structure from glassy to crystalline.

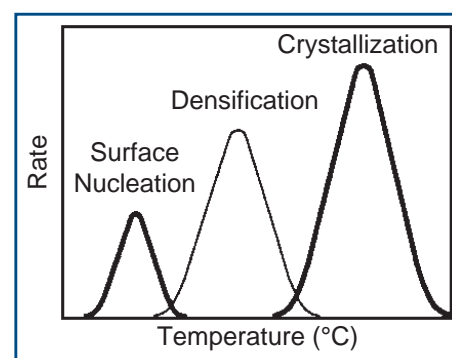
Glass-ceramic materials also can be produced through sintering of glass powders with a high specific surface. In the latter case, sintering and crystallization processes take place either one at a time or simultaneously. This renders the process extremely difficult to understand with respect to simple bulk devitrification.

The powders, once pressed, are sintered. Densification initially is obtained through viscous flow at temperatures slightly higher than the glass transition temperature. It does not follow the characteristic diffusion mechanism of crystalline powders.

When a glass powder is heated, its viscosity decreases, and every single grain changes its shape to spherical. A wetting liquid is formed between the particles. If temperature is high enough to maintain a certain degree of viscosity, the various grains start to be connected through necks.

The desired order of events in a glass-powder sintering process occurs when the sintering stage comes to an end before crystallization begins. Such behavior will hereafter be referred to as Type A. Those glass powders that present such behavior lead to extremely dense, low-porosity materials.

Unfortunately, the densification process does not always follow the sequence described. According to the glass composition or the heating rate followed, the crystallization stage may occur before or simultaneously with the sintering one. This may lead to porous and heterogeneous materials. Such behavior will hereafter be referred to as Type B.

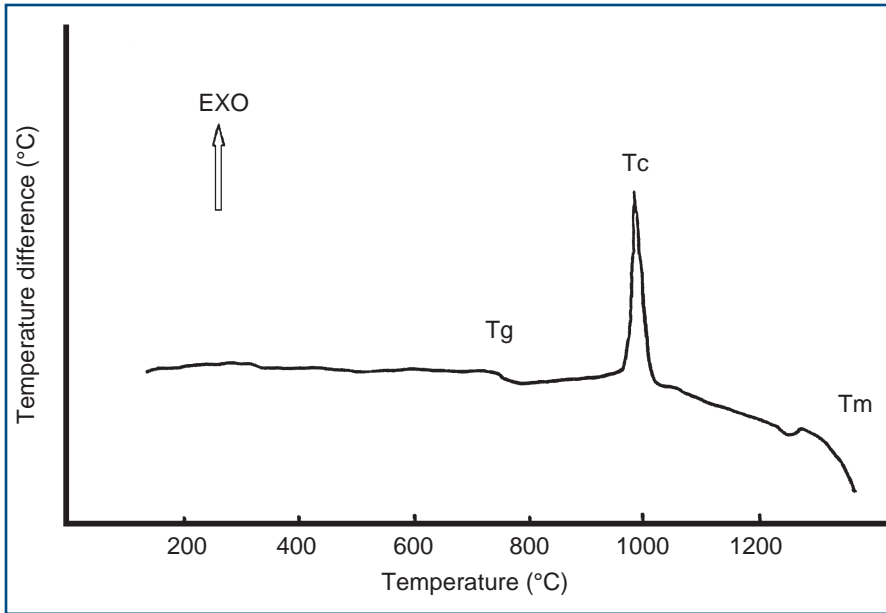


*Sintering behavior for obtaining good densification.*

This work attempts to predict the sintering process of glass-ceramic powders of different composition when heat-treated at a temperature higher than that of crystallization. Compositions investigated are of interest for use as frits for glazes, but the study may be extended to the sintering and crystallization process that leads to either monolithic or thick layer glass-ceramic materials.

The possibility of attaining such information beforehand has not been investigated previously. The sintering process of glass or glass-ceramic frits has always been approached with an experimental description of water absorption, linear shrinkage, density... curves as a function of temperature. From the industrial research point of view, such a time-consuming approach no longer keeps pace with market demands.

The approach suggested in this work may represent a simple and quick method for describing the sintering/crystallization process of different glass compositions. It combines data obtained by two thermal-analytical techniques commonly used in the traditional ceramic field; i.e., differential thermal analysis (DTA) and heating microscope analysis (HeMA).



DTA thermogram of a typical glass composition that originates a glass-ceramic during heating. Glass transition ( $T_g$ ), crystallization ( $T_c$ ) and melting ( $T_m$ ) temperatures are clearly visible.

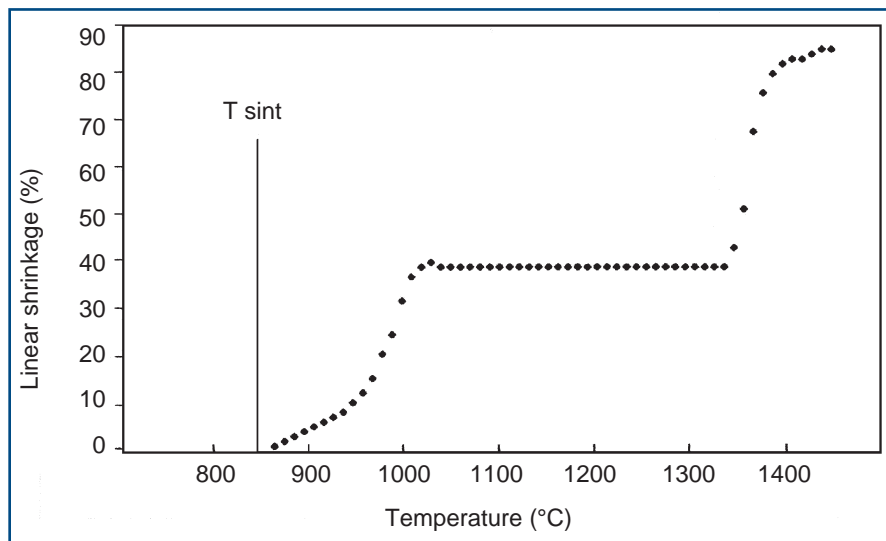
## Glass Compositions

The original glass composition, base-glass, is an industrial frit belonging to the wollastonite stability field of the glass-ceramic system  $\text{CaO-ZrO}_2\text{-SiO}_2$ .

Additions (5 mol%) of different oxides were made to the base-glass— $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$ —in order to obtain different quaternary systems that, hereafter, will be referred to as M-CZS. Each oxide was added to the industrial

frit, dry-mixed, melted in a mullite crucible at  $1450^\circ\text{C}$  for 30 min and then quenched rapidly in water.

The different sintering behaviors obtained were compared with the base-glass in terms of thermal curves from DTA and sintering curves from HeMA. DTA measurements (STA 409, Netzsch, Selb, Germany) were performed, using ~30 mg of glass powder (average particle size,  $20\ \mu\text{m}$ ) in a Pt crucible from 20 to  $1400^\circ\text{C}$ ,



Percent linear shrinkage vs. temperature as automatically evaluated by HeMA. The software records the beginning of sintering at a value of ~2% linear shrinkage and continuously registers dimension changes of the sample, even when its shape modifies during heating.

Composition	Behavior (Type)
Base	A
Li-CZS	A
Na-CZS	A
K-CZS	A
Ba-CZS	A
Mg-CZS	B
Zn-CZS	B
Ti-CZS	B
P-CZS	B

The glass-ceramic compositions are classified according to their sintering behavior by comparing the DTA and HeMA curves. Type A: sintering occurs before devitrification; Type B: devitrification occurs before complete densification.

with a heating rate of  $20^\circ\text{C}/\text{min}$ .

HeMA was performed on an identical glass powder, pressed to obtain small specimens (2-mm diameter, 2 mm high), positioned on an  $\text{Al}_2\text{O}_3$  plate. Black and white images of the sample profile were taken every  $20^\circ\text{C}$ , starting from a temperature of  $\sim 650^\circ\text{C}$  to a maximum temperature of  $1450^\circ\text{C}$ , with a heating rate of  $20^\circ\text{C}/\text{min}$ .

## Glass-Ceramics Compositions

Glass-ceramics were prepared by powder sintering and crystallization through heating treatments at different temperatures around the maximum crystallization temperature, as obtained from DTA for each composition.

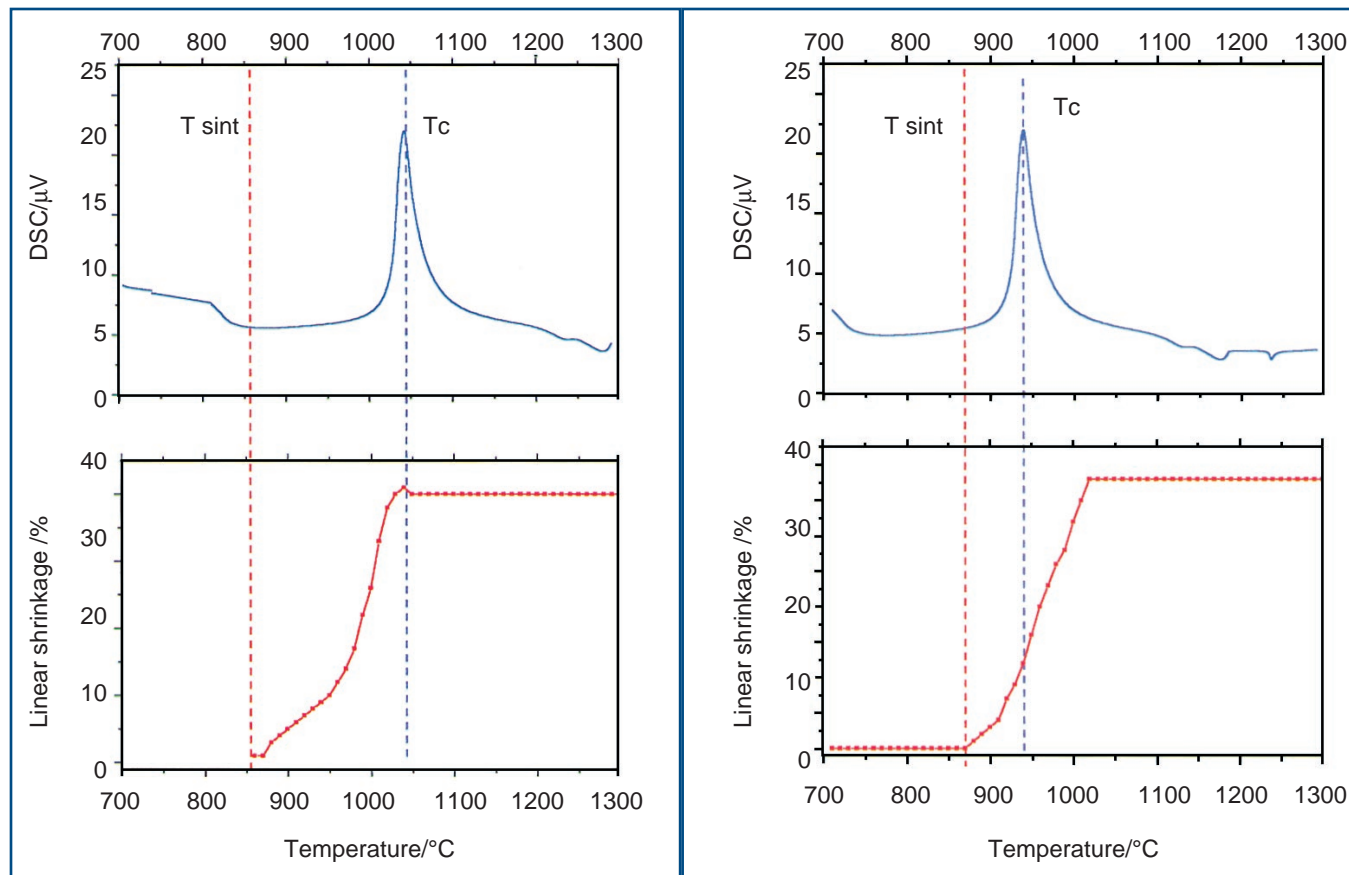
Powdered frits were obtained by wet milling to an average particle size of  $\sim 20\ \mu\text{m}$ . The powders were dried in an oven and humidified with 5 wt% water. They were then pressed at 30 MPa to obtain 10-g pellets of 40 mm diameter and 5 mm thickness.

Most of the M-CZS systems were subjected to heat treatments at 800, 900 and  $1000^\circ\text{C}$  with a heating rate of  $20^\circ\text{C}/\text{min}$ . Only the Li-CZS system was treated at 700, 800 and  $900^\circ\text{C}$ . Cooling time to room temperature was  $\sim 30$  min.

Glass-ceramic materials were characterized by XRD (Philips 3710) and SEM (Philips XL40).

## DTA and HeMA Data

The typical thermogram of a glass-ceramic composition points out the glass transition temperature ( $T_g$ ) inflexion point, the exothermic crystallization peak ( $T_c$ ) and the endothermic melting peak ( $T_m$ ). The last peak may or may not be present,



A comparison procedure was derived from overlapping the DTA and HeMA curves on the same temperature scale.

depending on the glass composition. Such behavior was observed for all the compositions presented in this work.

When plotting linear shrinkage (as obtained from HeMA) vs. temperature, the plot describes the starting stage of neck formation as a stage of moderate shrinkage. At higher temperatures, densification occurs, and shrinkage increases. All the phenomena previously described take place.

As for solid-state sintering, it is evident that linear shrinkage values do not increase after a certain temperature, but asymptotically verge to 100% densification. This means that, once a certain degree of compaction is reached, the thermal effect resulting from temperature increase no longer influences the sintering mechanism. The crystallization mechanism is then favored.

It is useful to compare, on the same temperature scale, DTA and HeMA plots to determine how composition may affect sintering and devitrification phenomena. In analyzing the plots obtained, two primary behaviors are exhibited by this procedure.

The first behavior is Type A. Type A describes those cases where the crystallization temperature ( $T_c$ ) falls at the beginning of the final sintering stage with asymptotic 100% densification. A glass powder that presents such behavior sinters before devitrification begins.

The second is Type B behavior. Type B describes those cases where  $T_c$  falls well before the maximum densification plateau. In glasses demonstrating such behavior, the crystallization process starts before complete densification is achieved.

### Effects of Oxide Additions

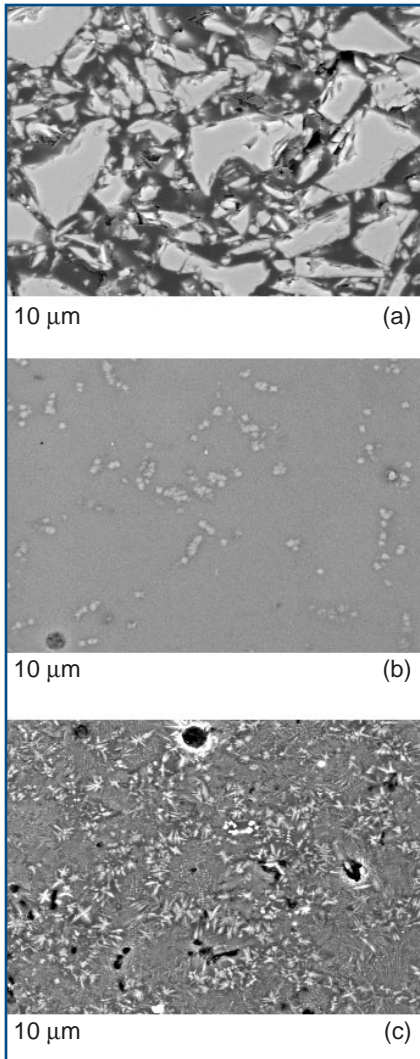
All the compositions studied in this work could easily be classified into Type A or B sintering behavior. Such classification also can be related with good approximation to the role played by the oxide when introduced into the silicate glass.

Simply by comparing DTA and HeMA curves, it was possible to illustrate how different oxides influence the behavior of the base-glass.

As a general rule, alkaline and alkaline-earth oxides, considered glass network modifiers, do not influence remarkably the glass behavior during devitrification. These oxides usually weaken the glass structure, inducing a viscosity decrease with a consequent lowering in  $T_g$ ,  $T_c$  and  $T_m$  values. With decreasing viscosity, all the diffusive processes strictly connected to crystallization are favored.

A different approach is necessary for  $P_2O_5$ ,  $TiO_2$ ,  $MgO$  and  $ZnO$ . In the case of  $P_2O_5$ , the observed Type B behavior can be explained in that this oxide is one of the major glass network formers. When introduced in a silica-based matrix that contains calcium ions, it can remarkably modify the glass network, reticulating it to a point that inhibits basic sintering mechanisms.

On the other hand,  $TiO_2$  is a well-known nucleating agent, promoting the devitrification process with respect to the sintering one. Such an effect may justify the decreased  $T_c$  value with respect to that of the base-glass.

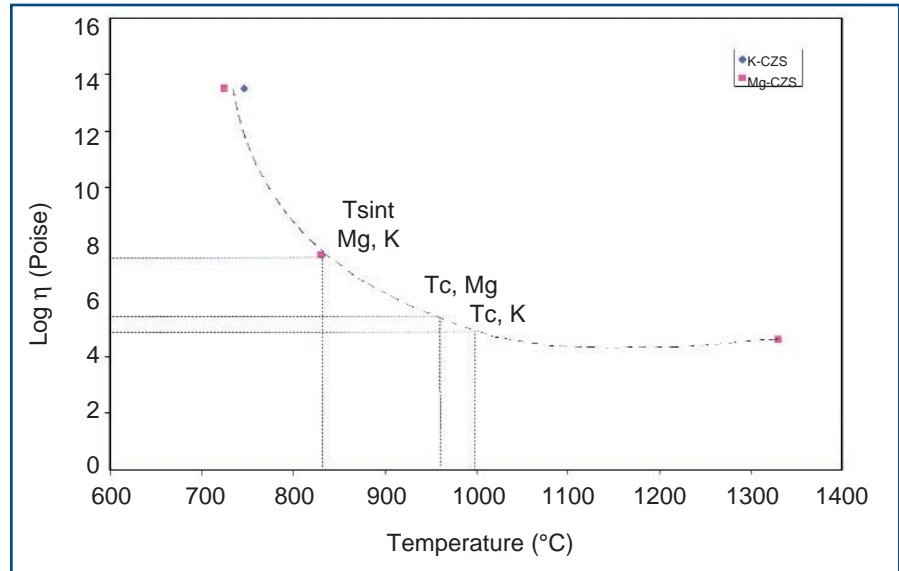


SEM observation of the microstructural evolution of the K-CZS system (Type A behavior) during the sintering process at (a) 800°C, (b) 900°C and (c) 1000°C.

Both MgO and ZnO are well-known network modifiers with high field-strength, producing a more ordered, glassy structure with respect to other network modifier oxides. They are colloquially called stabilizer oxides in industrial frit formulations. Their macroscopic effect is an increased glass viscosity with respect to other bivalent oxides, e.g., CaO and BaO. Stabilizer oxides render these two oxides similar to Phosphorous.

### Microstructure

SEM and XRD were used to characterize the microstructure of the glass-ceramic materials obtained by powder sintering at different soaking



Plot reporting log viscosity ( $\log \eta, P$ ) vs. temperature for two compositions—Mg-CZS and K-CZS. Crystallization temperatures indicated on the plot are derived from DTA and HeMA curves.

temperatures. This completed and supported data obtained from thermal analysis techniques.

Glass-ceramics with Type A behavior show a higher densification degree at lower temperatures while remaining mainly glassy. Crystallization starts from the surface of the glass grains and increases with increasing temperature.

At the highest temperature, samples are completely crystallized. From SEM observation, it is evident that after surface crystallization, the interior of the glass grain also devitrifies.

The two crystalline phases present different morphologies. These have been identified as a zirconium-calcium-silicate ( $2\text{CaO}\cdot 4\text{SiO}_2\cdot \text{ZrO}_2$ ) and, at higher temperatures, wollastonite ( $\text{CaO}\cdot \text{SiO}_2$ ).

The sintering behavior of Type B glass-ceramic compositions is completely different. Lower temperatures still present only reduced compaction, although we acknowledge the presence of slightly crystallized areas similar to those observed for Type A behavior.

For these Type B samples, maximum temperatures show the highest degree of crystallization, accompanied by extended porosity. Pore size also is slightly reduced with increasing temperatures from the beginning to the end of crystallization. It is evident that, although devitrification is complete, densification is not.

### Viscosity and Sintering

Further considerations concerning effects of different oxides on glass viscosity are possible through plotting viscosity values corresponding to  $T_g$ ,  $T_{\text{soft}}$  and  $T_{\text{semisphere}}$  vs. temperature.

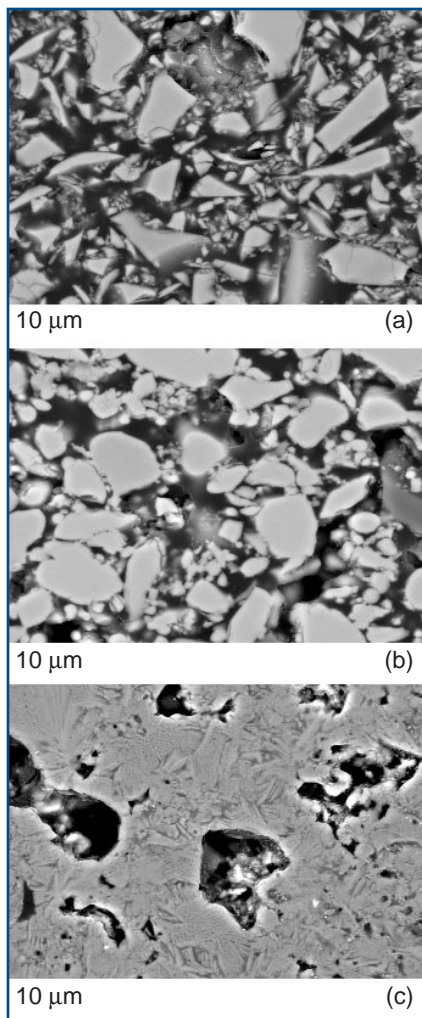
For all compositions, the viscosity value corresponding to the sintering temperature (as obtained by HeMA) falls close to the softening point ( $\log \eta = 7.6 P$ ). Reporting the crystallization temperature (from DTA curves) on the same plot indicates whether the influence of the oxide addition is primarily on viscosity/diffusion related mechanisms or on the nucleation mechanism.

### Observations

SEM observations confirmed the hypotheses on both Type A and Type B behavior. As expected, samples presenting Type A behavior were well-sintered with a low-porosity level.

To the contrary, those with Type B behavior demonstrated poor sintering and porosity levels with pores  $\sim 100 \mu\text{m}$  diameter. Although some compositions showed an intermediate behavior, a rough distinction could always be made.

The discriminating parameter related to the oxide effect seemed to be the capacity of the cation to decrease glass viscosity (Li, Na, K, Ba) or to favor crystallization (Mg, Zn, Ti, P).

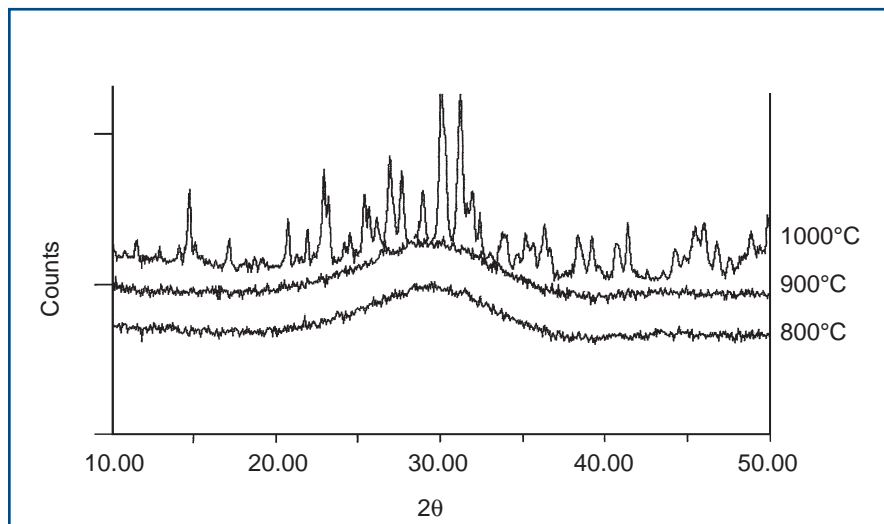


SEM observation of the microstructural evolution of the Mg-CZS system (Type B behavior) during the sintering process at (a) 800, (b) 900 and (c) 1000°C.

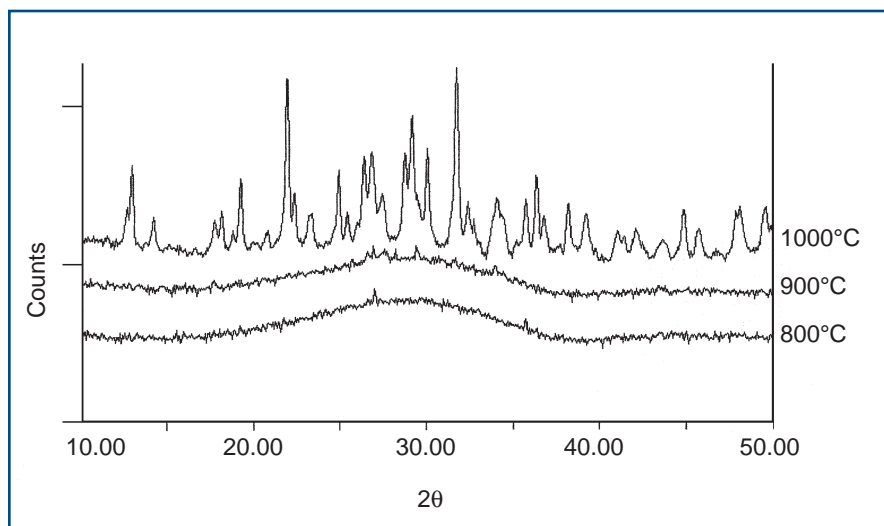
Some other variables should be taken into account when studying the sintering behavior of glass-ceramic frits using the method proposed in this work. The parameters that influence the sintering process are numerous and include:

- *Powder particle size.* The driving force of the sintering process is directly connected to the reduction of free energy. A fine particle size, therefore, enhances the process. Particle size distribution of powders is critical. A bimodal distribution leads to higher green densities than a monomial one.

- *Pressure.* Pressing conditions mainly affect the contact surface per volume unit; elastic and plastic deformations are a result of gas inclusion. The higher the pressure, the higher the



XRD patterns of K-CZS system (Type A behavior) treated at different soaking temperatures.



XRD patterns of Mg-CZS glass-ceramic (Type B behavior) do not significantly differ from those seen for the K-CZS system, even if a weak crystallization is already present at 900°C. At 1000°C, the sample appears completely crystallized.

green density and the lower the linear shrinkage of the sintered body.

- *Temperature and heating cycles.* All structural changes connected to the sintering process depend on mechanisms of transport, most of which are diffusive processes.

In order to have consistent results, powder particle size distribution and the powder forming process should be maintained constant during both DTA and HeMA analysis, even though HeMA results are less sensitive to such a parameter than DTA.

It is important to always use the

same degree of compaction of powders used for both analytical techniques. Finally, the most important variable to take into account is the heating rate degree. ■

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