Extended Report
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KINETICS OF PHASE TRANSFORMATION IN GLASS FORMING SYSTEMS
NASA Contract: NAG8-898

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Task Objectives:

The objectives of this research were to (1) develop computer models for realistic simulations of nucleation and crystal growth in glasses, which would also have the flexibility to accomodate the different variables related to sample characteristics and experimental conditions, and (2) design and perform nucleation and crystallization experiments using calorimetric measurements, such as differential scanning calorimetry (DSC) and differential thermal analysis (DTA) to verify these models.

The variables related to sample characteristics mentioned in (1) above include size of the glass particles, nucleating agents, and the relative concentration of the surface and internal nuclei. A change in any of these variables changes the mode of the transformation (crystallization) kinetics. A variation in experimental conditions includes isothermal and nonisothermal DSC/DTA measurements. Isothermal kinetic studies yield reasonably accurate information about the mode of transformation and the activation energies of nucleation and growth, but nonisothermal measurements have several advantages. The nonisothermal measurements are easier to perform and less time consuming, and they can probe the kinetics of transformation over a different, generally higher, temperature range than is possible from isothermal methods. However, the thermoanalytical models prsently used to analyze the nonisothermal kinetic data are considered to be fundamentally flawed, since they are based on erroneous assumptions for the temperature dependence of the effective rate constants, generally, resulting in misinformation about the transformation processes. This research would lead to develop improved, more realistic methods for analysis of the DSC/DTA peak profiles to determine the kinetic parameters for nucleation and crystal growth as well as to assess the relative merits and demerits of the thermoanalytical models presently used to study the phase transformation in glasses.

The present research is a part of a collaborative research program supported by NASA through two separate contracts. The experimental work is conducted at the University of Missouri-Rolla (NASA Contract NAG8-898, PI: C. S. Ray) and the theoretical work is conducted at the Washington University in St. Louis (NASA Contract NAG8-873, PI: K. F. Kelton).

Benefit or Necessity of Microgravity:

Existing experimental evidences on solidification of glass forming melts in microgravity point to the importance of investigating the kinetics of nucleation and crystallization in a more generalized and realistic way. For example, glasses prepared in microgravity are reported to be more chemically homogeneous and more resistant to crystallization than identical glasses

prepared on earth. These results indicate that the size, number density, and distribution of nuclei, and, hence, the nucleation mechanism, are different in glasses prepared in space and on earth. To verify these apparently surprising observations, realistic thermoanalytical models as well as experimental data on phase transformation in glasses prepared in space are needed.

Results to-Date:

1. Nucleation/Crystallization of $Na_2.2Cao.3SiO_2$ (NC_2S_3) Glass:

A previously developed experimental technique[1] which uses nonisothermal DSC/DTA and which was justified theoretically by others[2,3], was used to determine the nucleation rate-temperature like curve for the NC_2S_3 glass. In this technique, a small amount ($\sim$ 20 to 40 mg) of relatively large glass particles ($>$ 400 μm) are first nucleated in the DSC/DTA furnace at different temperatures for an arbitrarily chosen time (typically 2 to 4 h) and then heated at a selected rate (normally 15°C/min) until crystallization is complete. A plot of the inverse of the temperature at the crystallization peak maximum, $1/T_p$, or the height of the peak at T_p, $(\delta T)_p$, against the temperature, T_n, at which the glass particles are nucleated, yields a curve similar in shape to that of the classical nucleation rate curve, I vs. T_n. The values of $(\delta T)_p$ and $1/T_p$ for the NC_2S_3 glasses containing 0.1 wt% Pt, 0.5 wt% Ag_2O, or 2.0 wt% P_2O_5 are shown in Fgs. 1 and 2 as a function of T_n along with the values for the NC_2S_3 base glass, which show that unlike the lithium disilicate (LS_2) glass, the $(\delta T)_p$ and $1/T_p$ plots as a function of T_n for the NC_2S_3 glasses do not agree with each other. For a better comparison of these two plots, see Figs. 3 and 4, which are the normalized versions of Figs 1 and 2, respectively. For the LS_2 glass, these two plots not only agree with each other, they also agree with the I vs. T_n curve for the LS_2 glass determined by classical method[1] and with the $(\delta T)_p$ vs. T_n curve calculated through computer simulation[2,4].

As shown in Figs. 2 and 4, the plots of $1/T_p$ vs. T_n are nearly the same for all the doped and undoped NC_2S_3 glasses. The temperature range for nucleation, 545-665°C, and the temperature for maximum nucleation, $\sim$ 595°C, determined from these plots (Figs 2 or 4) are also in excellent agreement with those for the NC_2S_3 glass determined by conventional method[5]. These results suggest that the $1/T_p$ vs. T_n plot correctly represents the I vs T_n curve for the NC_2S_3 glass, but the $(\delta T)_p$ vs. T_n plot does not. The reason for this is attributed to an overlap between the I and U (crystal growth rate) curves for this glass, which does not occur for the LS_2 glass where the I and U curves are separated. If a glass is nucleated at a temperature T where the I and U curves overlap, part of the glass can crystallize and the total number of nuclei available for further crystallization can decrease. This, in turn, will decrease $(\delta T)_p$ at all temperatures within the region of overlap and, consequently, the temperature spread and the peak of the $(\delta T)_p$ curve on the temperature scale will be lower than what it would be in the absence of any overlap between I and U. On the otherhand, $1/T_p$ depends primarily on the concentration of nuclei and is independent of the previously described effect of overlap between I and U, provided the glass does not crystallize completely during nucleation heat treatment.

2. Calculation of $(\delta T)_p$:

To verify the above conclusion that the shape of the $(\delta T)_p$ vs. T_n curve depends upon the overlap between I and U, calculations were made for a hypothetical glass at diffrent degrees of overlap between two arbitrarily chosen I and U curves. The following equation

$$(\delta T)_p = KVIt [1 - (1/3)\pi IU^3t^4] \quad \dots \quad \dots \quad \dots \quad (1)$$

that relates $(\delta T)_p$ with I and U was developed assuming $(\delta T)_p$ is linearly proportional to the total number of nuclei present in the glass. Here, V is the volume of the sample, t is the time for nucleation heat treatment prior to DTA scan, and K is a constant. When there is no overlap

between I and U at the chosen nucleation temperature, the second term in eqn. 1 is zero, and the functional dependence of $(\delta T)_p$ on T_n is same as that of I on T_n, such as what is observed for the LS_2 glass. When I and U overlap at the temperature of nucleation, the second term in eqn.1 is no longer zero, and $(\delta T)_p$ is smaller than what it should be in the absence of overlap.

The calculated values of $(\delta T)_p$ at different degrees of overlap between I and U is shown in Fig. 5 as a function of nucleation temperature. Fig. 5 shows that the spread of the $(\delta T)_p$ vs. T_n curve on the temperature axis and the temperature at the peak maximum both decrease with increasing overlap between I and U. Comparing these curves with the experimental curves in Fig. 4, it is clear that a maximum overlap between I and U curves occurs for the NC_2S_3 glass which is doped with platinum. For the glass doped with P_2O_5, the overlap between I and U is even smaller than that for the NC_2S_3 base glass. This result suggests that P_2O_5 in the NC_2S_3 glass does not act as a nucleating agent, rather it improves glass formation in the NC_2S_3 glass.

3. Dependence of $(\delta T)_p$ on DTA Scan Rate:

In crystallization measurements using DTA the glass sample is scanned at different constant heating rates until it crystallizes. This means that the temperature range where nucleation can occur is scanned also at different rates, which allows the glass to be nucleated for different time prior to crystallization. Consequently, the concentration and, hence, the total number nuclei in the glass sample may be different when scanned at different rates, which may cause a change in the DTA peak height and the temperature at the peak maximum.

The effect of nucleation heating rate on the $(\delta T)_p$ was investigated using a LS_2 glass. Since the nucleation temperature for LS_2 glass ranges from 400 to 500°C, the glass sample was first heated at a high heating rate (~ 100°C/min) from room temperature to about 400°C. After stabilizing at 400°C for a brief period of time (3 to 5 min), the sample was heated to 500°C using constant different heating rates (Nucleation Heating Rate, ϕ_n: 0.5, 1, 2, 4, 6, 10, or 15°C/min) and then heated at a constant 15°C/min heating rate until the crystallization completed. The particle size and the amount of glass sample were kept unchanged for different measurements.

The DTA crystallization peak height, $(\delta T)_p$, for the LS_2 glass obtained at a constant crystallization heating rate, 15°C/min, is shown in Fig. 6 as a function of nonisothermal nucleation heating rate, ϕ_n (solid circles). The $(\delta T)_p$ decreases initially with increasing ϕ_n indicating the formation of a less number of nuclei as the nucleation temperature zone for this glass is scanned at a higher heating rate. This is what is expected since with increasing heating rate, the glass is allowed to nucleate for a shorter average time, which results in forming a less number of nuclei. No appreciable change in $(\delta T)_p$ for this glass is observed when ϕ_n exceeds about 3°C/min, which suggests that for a heating rate > 3°C/min an embryo in the LS_2 glass does not get sufficient time to form a critical size nucleus. This critical value of ϕ_n could be important for many practical reasons, since it ensures a heating rate above which no new nuclei form in a glass.

Also shown in Fig. 6 (open squres) are the values of $(\delta T)_p$ for the LS_2 glass measured previously[1] by isothermal nucleation at 453°C (temperature for maximum nucleation rate) followed by crystallization at the same 15°C/min heating rate. Interestingly, the $(\delta T)_p$-value of a sample nucleated isothermally at the maximum nucleation rate temperature for a particular time, t, is in excellent agreement with that of the sample nucleated nonisothermally at a rate that requires the same time t to scan the temperature zone for nucleation. For example, the temperature range for nucleation for the LS_2 glass is ~ 75°C (425 to 500°C), and it takes ~ 150 min to scan this region at a ϕ_n of 0.5°C/min. An equal amount of sample with same particle size of this LS_2 glass yields nearly the same peak height when nucleated either nonisothermally at

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0.5°C/min or isothermally at 453°C for 150 min followed by crystallization at 15°C/min.

4. Nucleation Rate Curve for the LS₂ Glass by Dielectric Constant Measurements:

Since the dielectric constant of a material depends, in part, on crystallinity of the sample and, hence, upon the concentration of nuclei prior to crystallization, attempts were made to determine the nucleation rate-temperature like curve for a LS_2 glass by dielectric constant measurements. Glass samples, ~ 1 mm thick, were nuleated isothermally at different temperatures for 3 h and then crystallized at 660°c for 15 min. Both surfaces of the crystallized samples were polished with 1 μm alumina powder and then coated with gold in vacuum. The dielectric constant, ϵ, and the tanδ loss of the samples were measured at 1 kHz using a HP-4270 automatic capacitance bridge. Both ϵ and tanδ decrease initially and then increase with increasing nucleation temperature, yielding a minima at about 450°C which is close to 453°C temperature for the maximum nucleation rate of this LS_2 glass. A plot of $1/\epsilon$ against the nucleation temperature is shown in Fig. 7, the shape of which closely resembles that of the classical nucleation rate curve for the LS_2 glass. This technique (measuring ϵ and tanδ), thus, appears to be a feasible one for determining the temperature range for nucleation and the temperature for maximum nucleation in a glass.

References:

1. C. S. Ray and D. E. Day, "Determining the Nucleation Rate Curve for a Lithium Disilicate Glass by Differential Thermal Analysis", J. Am. Ceram. Soc., **73**, 439 (1990).
2. K. F. Kelton, "Estimation of the Nucleation Rate by Differential Scanning Calorimetry", J. Am. Ceram. Soc., **75**, 2449 (1992).
3. M. C. Weinberg, "Interpretation of DTA Experiments Used for Crystal Nucleation Rate Determination", J. Am. Ceram. Soc., **74**, 1906 (1991).
4. C. S. Ray and D. E. Day, "Nucleation and Crystallization in Glasses as Determined by DTA", Ceramic Transactions, vol 30, pp 207-223 (1993).
5. E. D. Zanotto and A. Galhardi, "Experimental Test of the General Theory of Transformation Kinetics: Homogeneous Nucleation in a $Na_2O.2CaO.3SiO_2$ Glass", J. Non-cryst. Solids, **104**, 73 (1988).

Present and Future Work:

1. Effect of DTA scan rate on nucleation for the NC_2S_3 glass.
2. Dependence of DTA peak height and peak temperature on particle size of the LS_2 glass with and without nucleating agents.
3. Estimation of nucleation rate, I, at different temperatures from $(\delta T)_p$ vs. T_p plots for the LS_2 glass.
4. Study the usefulness of a recently developed technique for determining the nucleation rate-temperature like curves from dielectric constant and tanδ loss measurements using other glasses such as $Na_2O.2SiO_2$ and $Bao.2SiO_2$.

Presentation/Publication:

The following technical presentations and publications have resulted from this research.

A. Presentations:

1. C. S. Ray, D. S. McIntyre, and D. E. Day, "Studies on Nucleation and Crystallization of Glasses by DTA", 94th Annual Meeting of the American Ceramic Society, Minneapolis, MN, 12-16 April 1992.
2. C. S. Ray and D. E. Day, "Nucleation and Crystallization in Glasses as Determined by

DTA", The 4th International Symposium on Nucleation and Crystallization in Glasses and liquids held in Evergreen Resort, GA, 16-19 August 1992.

3. T. S. Cull, K. F. Kelton, and C. S. Ray, "Numerical Simulation of Nonisothermal Crystallization of Lithium Disilicate Glass", Midwest Solid State Conference, University of Missouri-Columbia, Columbia, MO, September 1993.

4. K. F. Kelton, T. S. Cull, C. S. Ray, and D. E. Day, "Computer Simulation of Nonisothermal Phase Transformations", 8th Annual Symposium on Microgravity Science and Space Processing, Reno, Nevada, 10-13 January 1994.

5. W. Huang and C. S. Ray, "Nucleation Rate Curve for a $Li_2O.2SiO_2$ Glass by Dielectric Measurements", 96th Annual Meeting of the American Ceramic Society, Indianapolis, IN, 24-28 April 1994.

6. K. L. Narayan, T. S. Cull, K. F. Kelton, and C. S. Ray, "Heterogeneous Nucleation in Lithium Disilicate Glass", 96th Annual Meeting of the American Ceramic Society, Indianapolis, IN, 24-28 April 1994.

Publications:

1. C. S. Ray and D. E. Day, "Nucleation and Crystallization in Glasses as Determined by DTA", Ceramic Transactions: Nucleation and Crystallization in Liquids and Glasses (Ed: M. C. Weinberg), vol. 30, 207-223 (1993).

2. W. Huang, C. S. Ray, and D. E. Day, "The Determination of Nucleation rate Curve in the Crystallization process of Glasses from DTA Technique", Journal of Shanghai Institute of Building Materials (in Chinese), 6 (3), 187-195 (1993).
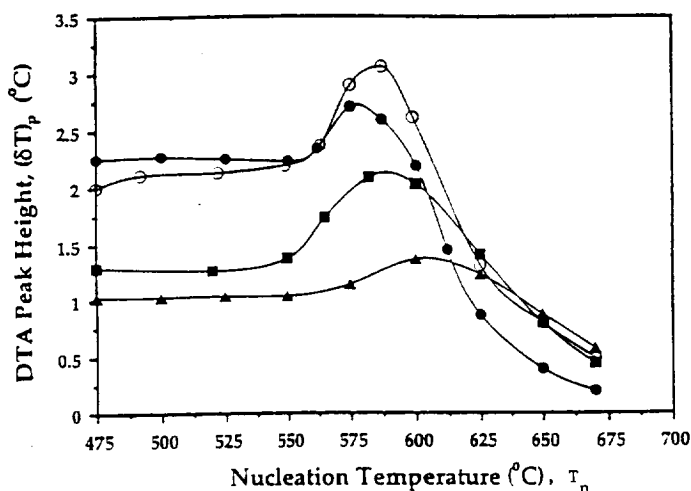

Fig.1: DTA peak height for the NC_2S_3 glass containing different dopants as a function of T_n for 3 h.
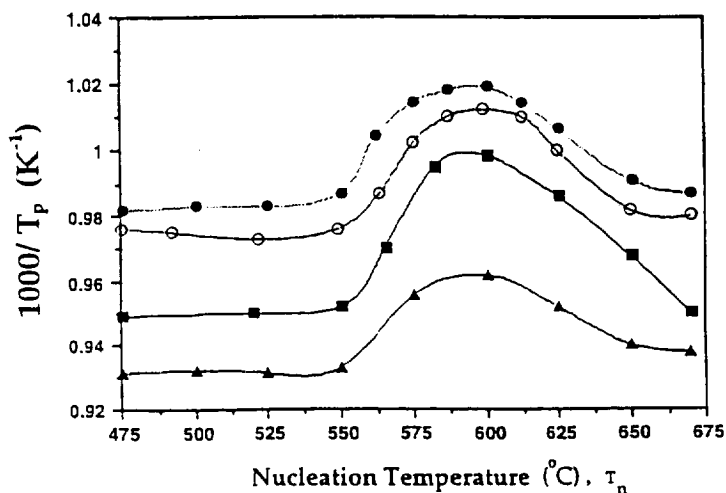
Fig.2: Inverse of DTA peak temperature for the NC_2S_3 glass containing different dopants as a function of T_n for 3 h.

For both figures: crystallization heating rate, 15°C/min; particle size, 425-500 μm; sample weight, 30 mg. O, base glass; •, o.1 wt% Pt; ■, 0.5 wt% Ag_2O; ▲, 2.0 wt% P_2O_5.
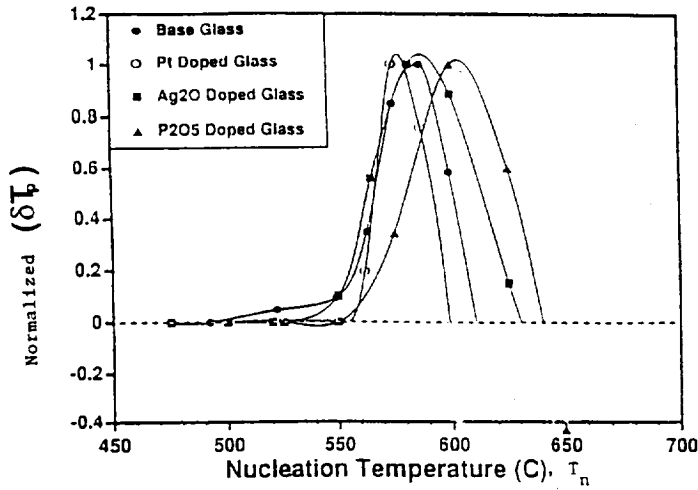
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Fig.3: Same as Fig.1, but the data were normalized with respect to those for the as-quenched, unnucleated glass.
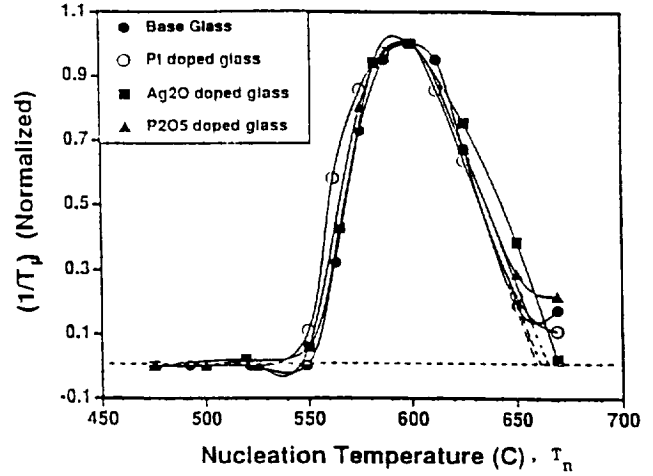
Fig.4: Same as Fig.2, but the data were normalized with respect to those for the as-quenched, unnucleated glass.
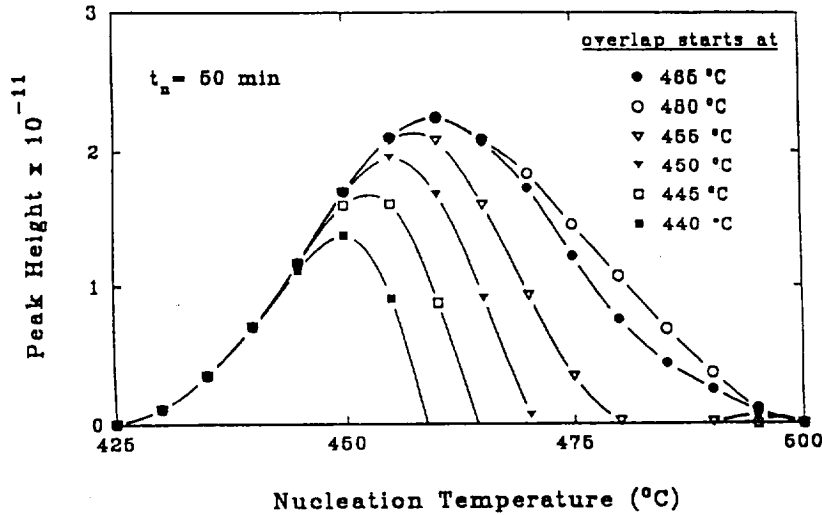

Fig.5: Calculated DTA peak height (eqn.1) for a hypothetical glass as a function of nucleation temperature for different overlaps of I and U. The spread (on temperature axis) and the temperature at the maxima of these curves clearly decrease with increasing overlap between I and U.
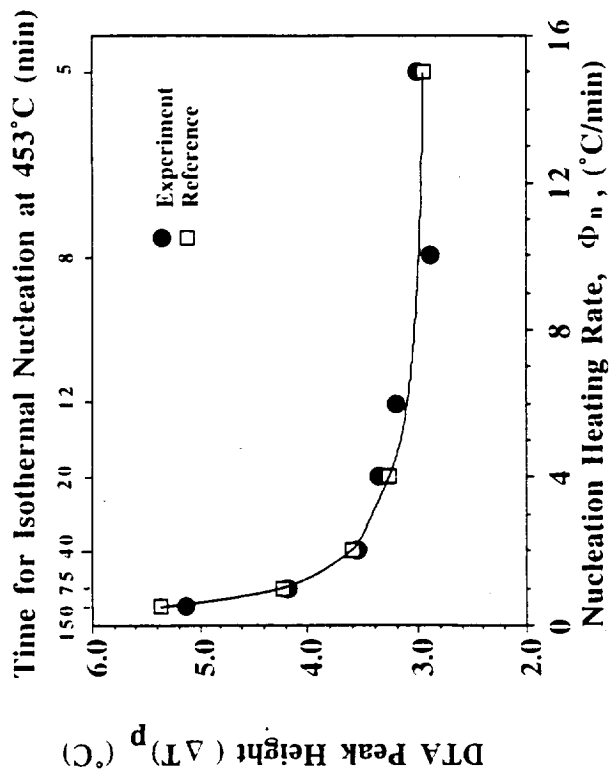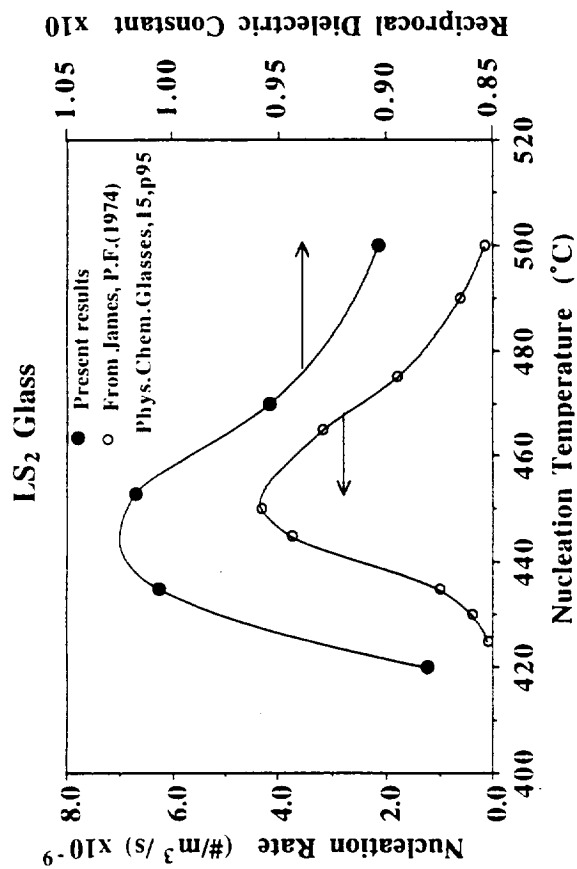
Fig.7: Reciprocal of the Dielectric constant at 1 kHz for a lithium disilicate glass as a function of nucleation temperature for 3 h. Crystallization temperature: 660°C for 15 min. For comparison, the nucleation rate curve for the lithium disilicate glass measured conventionally is also given.

Fig.6: DTA peak height ($\bullet$, Experiment) for the lithium disilicate glass as a function of nucleation heating rate. The open squares (Reference) are the peak heights for the same glass nucleated isothermally at 453°C prior to crystallization. The time for isothermal nucleation (given at the top) is the same as what is required to scan the nucleation temperature range at a rate given by the horizontal axis for the reference point. Sample wt.: 35.9 mg, particle size: 425-500 μm, crystallization heating rate: 15°C/min.