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KINETICS OF PHASE TRANSFORMATIONS IN GLASS FORMING SYSTEMS

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A. WORK COMPLETED

1. *Nucleation Rate for an $Li_2O.2SiO_2$ (LS_2) Glass from DTA Peak Height Measurements:*

We demonstrated previously(1,2) that a nucleation rate like curve for a glass could be determined from the functional dependence of the maximum height of its DTA crystallization peak, $(\delta T)_p$, on the nucleation temperature, T_n. This experimental method was also justified theoretically by other investigators(3,4). This nucleation rate like curve provides information for the temperature range where nucleation for the glass can occur and the temperature where the nucleation rate is a maximum. But, this curve does not provide information for the nucleation rate, I, for the glass at different temperatures. A method for estimating I at different temperatures from $(\delta T)_p$ was developed using a $Li_2O.2SiO_2$ (LS_2) glass.

In this method, the $(\delta T)_p$ for the LS_2 glass prenucleated isothermally at a particular temperature (443°C in this case) for different times was first measured maintaining the sample weight (~40 mg), DTA scanning rate (15°C/min) and sample particle size (425-500 μm) constant for different measurements, see Fig 1. As expected, $(\delta T)_p$ increased with increasing nucleation time due to the formation of increasing number of internal nuclei in the glass. The $(\delta T)_p$ for the as-quenched LS_2 glass doped with 0.001 wt% and 0.005 wt% platinum was then measured using the same sample weight, particle size and DTA scanning rate and compared with that of the internally nucleated glassses. Assuming (1) the concentration of (initial) quenched-in nuclei is same in both doped and undoped glasses and (2) an internal necleus produces the same DTA peak height as that of a heterogeneous nucleus, the internal nucleation rate, I, at a particular temperature is calculated from the concentration of heterogeneous nuclei in the doped glass. Assumption (1) is considered reasonable, since all the glasses used in these DTA measurements were melted and quenched in the same way. Assumption (2) is also believed to be valid unless the crystal growth rate on a heterogeneous nucleus is different from that on a homogeneous nucleus, of which no experimental or theoretical evidence is available. The use of two data points in Fig. 1 and two dopant (platinum) concentrations in the glass automatically eliminates the effect of quenched-in nuclei on the DTA crystallization peak height. Calculations for determining I at 443°C for the LS_2 glass are given below, as an example.

Fig 1 shows that $(\delta T)_p$ for the as-quenched LS_2 glass doped with 0.001 wt% and 0.005 wt% Pt is same as that of the undoped glass internally nucleated at 443°C for 4 h and 7 h, respectively. The increase in $(\delta T)_p$ caused by changing the nucleation time from 4 h to 7 h of the undoped glass is for the crystallization of an excess number of internal nuclei, N_{in}, developed due to 3 h of longer nucleation. This number N_{in} is considered same as the number of heterogeneous nuclei, N_{hn}, created by changing the platinum concentration from 0.001 wt% to 0.005 wt%.

If N_{pt} is the number of platinum particles added to the glass when the wt% platinum concentration increases from 0.001 to 0.005 i.e, by 0.004 wt% (= C_{pt}) and n_{pt} is the number of platinum particles in a critical size nucleus, then

$$N_{hn} = N_{pt} / n_{pt} \quad \dots \quad \dots \quad \dots \quad (1)$$

Now, N_{pt} can be written as

$$N_{pt} = (C_{pt} \, . \, w_s \, . \, N) / (100 \, . \, A_{pt}) \quad \dots \quad \dots \quad \dots \quad (2)$$

where, C_{pt} = 0.004
w_s = weight of the glass sample = 40 mg = 40×10^{-3} g
N = Avogadro Constant = 6.02×10^{23}
A_{pt} = Atomic weight of platinum = 195.1

Also,

$$n_{pt} = (V_c / V_{pt}) = (R_c / R_{pt})^3 \quad \dots \quad \dots \quad \dots \quad (3)$$

where, V_c = volume of a critical size heterogeneous nucleus
V_{pt} = volume of a platinum particle
R_c = average radius of a critical size heterogeneous nucleus
= 0.2×10^{-6} m (Cronin and Pye, JNCS 84, 196 (1986))
R_{pt} = average radius of a platinum ion = 0.725×10^{-10} m

The internal nucleation rate, I, which is the number of nuclei developed per unit volume per unit time can be given as:

$$I = N_{in} / (v_s \, . \, t_n) = (N_{in} \, . \, d_s) / (W_s \, . \, t_n) \quad \dots \quad \dots \quad (4)$$

where, N_{in} = N_{hn} (calculated using eqn. 1)
d_s = density of the glass sample = 2.54 g/cm^3 (measured)
v_s = volume of the glass sample

t_n = time for nucleation treatment = 3 h (in this case)
= 108,00 seconds

Using eqns (1), (2), and (3), eqn (4) can be written as,

$$I = (C_{pt} \,.\, N \,.\, d_s \,.\, R_{pt}^3) \,/\, (100 \,.\, A_{pt} \,.\, t_n \,.\, R_c^3) \quad \ldots \quad (5)$$

Using the values for different symbols given above for the LS_2 glass, eqn (5) yields,

I (at 443°C) = 1.36×10^9 m^{-3} s^{-1} which is in excellent agreement with the 2.57×10^9 m^{-3} s^{-1} value determined by James et al (Phys. Chem. Glasses 15, 95 (1974)) for the LS_2 glass using conventional method. The slightly lower value of I determined by the present method compared to that determined by conventional method may be due to the reason that the size of a critical nucleus has been overestimated in the present calculations. Nevertheless, the present method provides a rapid and useful means to obtain a close estimate for the nucleation rate of a glass at a particular temperature.

This value of I at 443°C can now be used to determine the approximate nucleation rates at other temperatures. The difference between the measured $(\delta T)_p$ of the glass samples nucleated at a temperatures, T, and that of the as-quenched glass should be proportional to the number of internal nuclei developed due to nucleation treatment at T. Denoting that difference as $\Delta(\delta T)_p$, we can write,

$$\Delta(\delta T)_p = \left|(\delta T)_p\right|_T - \left|(\delta T)_p\right|_{Quenched} = K.N_{in}$$

$$= K.I.v_s.t_n = (K.I.w_s.t_n)/d_s \quad \text{(see eqn. 4)} \quad \ldots \quad (6)$$

where, K is a constant.

If the sample weight (w_s) and time for nucleation at different temperatures (t_n) are kept constant for different DTA measurements, then eqn. 6 can be written as (d_s is constant, since the same LS_2 glass was used):

$$\Delta(\delta T)_p = K'.I \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

$$K' = (K.w_s.t_n)/d_s$$

Using the value of I (=1.36×10^9, calculated above) and measured $(\delta T)_p$ for the as-quenched glass (=4.57) and that of the glass nucleated at 443°C for 4h (=6.71), we get the value of the constant K' as:

$$K' = (6.71 - 4.57)/(1.36 \times 10^{9})$$
$$= 15.735 \times 10^{-10}$$

Assuming K' and, hence, K, to be temperature independent (which may not be a reasonable assumption), the value of I at a few selected temperatures has been calculated using eqn. 7 and is shown in Table 1.

Table 1: Nucleation Rate, I, of the LS_2 glass determined in the present investigation at a few selected temperatures.

Temp. °C	$(\delta T)_p$	$\Delta(\delta T)_p$*	I, (# m^{-3} s^{-1}) x 10^{-9}	
			Present Result	James et al**
420	5.44	0.87	0.55	------
443	6.71	2.14	1.36	2.57
460	14.24	9.67	6.15	3.94
475	12.20	7.63	4.85	1.78
495	5.72	1.15	0.73	0.32

* The $(\delta T)_p$ for the undoped as-quenched glass is 4.57.
** Phys. and Chem. of Glasses **15**, 95 (1974).

Except for the 443°C temperature which was used as the reference temperature to calculate I, the values of I determined by the present method is higher than those determined by conventional method at other higher temperatures, see Table 1. The reason for this difference is not clearly understood at this time, but may be due to the reasons that (1) the assumption that K is independent of temperature is not justified and (2) the dependence of the size of a critical nucleus on temperature (which increases with increasing temperature) has not been accounted for in the present calculations. Considering the size dependence of the critical nucleus on temperature, further calculations to determine I at different temperatures for the LS_2 glass are continuing.

2. *Determining Nucleation Rate Like Curve for the LS_2 Glass from Dielectric Measurements:*

The dielectric constant (ϵ) and loss factor ($\tan\delta$) of a glass-ceramic depend, in part, upon the amount of crystallinity which, in turn, depends upon the nucleation density in the starting glass. It is, therefore, expected that ϵ and $\tan\delta$ should have a relationship with nucleation density and, hence, on the nucleation rate, I, of the glass. Based on this idea, ϵ and $\tan\delta$ for lithium disilicate (LS_2) glass-ceramics were measured at 1 kHz using a HP-4270 automatic capacitance bridge. First, the LS_2 glass was prepared by melting an appropriate batch at 1480°C for 4h and quenching the melt between iron plates. The glass was then polished at both surfaces using 1 μm alumina powder and glass samples of ~ 8 mm diameter and 1 mm thick were prepared for measurements. These samples were nucleated isothermally at different temperatures, T_n, for different times, t_n, and then crystallized at 660°C for 15 min. The glass-ceramics so prepared were coated at both surfaces with gold in vacuum (to ensure good electrical contact) before measuring ϵ and $\tan\delta$.

The dielectric constant, ϵ, and the loss factor, $\tan\delta$, of the LS_2 glass ceramics which were prepared by nucleating the glass at 453°C and crystallizing at 660°C for 15 min are shown in Figs. 2 and 3, respectively, as a function of nucleation time at 453°C. With increasing nucleation time, the number of nuclei and, hence, the percent crystallinity in the sample increase. Figs. 2 and 3 show that ϵ and $\tan\delta$ both decrease with increasing crystallinity in this LS_2 glass-ceramic, which is, probably, expected since increasing crystallinity increases the number of (structurally arranged) crystals and decreases the number of mobile ions, lithium in this case.

The values of ϵ and $\tan\delta$ of the glass ceramics prepared by nucleating at different temperatures, T_n, for a fixed time (3 h) and crystallizing at 660°C for 15 min have been plotted in Figs. 4 and 5 as a function of T_n. Both ϵ and $\tan\delta$ initially decrease with increasing T_n , yield a minima at about 450°C, and then increase with further increase in T_n. A plot of $1/\epsilon$ vs T_n is shown in Fig. 6, the shape of which closely resembles the shape of the nucleation rate curve for the lithium disilicate glass. For comparison the nucleation rates, I, for the lithium disilicate glass at different temperatures determined by traditional method (James et al, Phys. and Chem. of Glasses, **15**, 95 (1974)) have also been plotted in Fig.

6. which clearly shows the close resemblance between the shapes of these two curves ($1/\epsilon$ vs T_n and I vs T_n). Like the I vs T_n curve, the $1/\epsilon$ vs T_n curve yields a maxima at about 450°C (temperature at which the nucleation rate is highest) and a temperature range, from about 420° to 500°C, where nucleation can occur for this lithium disilicate glass. Thus, measuring the dielectric constant or the loss factor for glass ceramics prepared by nucleating at different temperatures for different times and crystallizing at a higher temperature for a short time, also appears to be a feasible method for determining the nucleation rate like curve for the base glass. Measurements of ϵ and $\tan\delta$ for the LS_2 glass ceramics prepared by nucleating at a particular temperature for a fixed time and crystallizing at different temperatures for different times are continuing.

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. C. S. Ray and D. E. Day, "Nucleation and Crystallization in Glasses as Determined by DTA", Ceramic Transactions, **30**, 207 (1993).
3. K. F. Kelton, "Estimation of the Nucleation Rate by Differential Scanning Calorimetry", J. Am. Ceram. Soc., **75**, 2449 (1992).
4. M. C. Weiberg, "Interpretation of DTA Experiments Used for Crystal Nucleation Rate Determination", J. Am. Ceram. soc., **74**, 1906 (1991).

B. WORK IN PRPGRESS/PLANNED

1. *Continue measurements and calculations for quantitative determination of the nucleation rates for a lithium disilicate glass at different temperatures.*
2. *Continue measurements of the dielectric constant and loss factor for lithium disilicate glass ceramics.*
3. *Measure the effect of glass particle size on DTA peak height and temperature for a lithium disilicate glass. This investigation may lead to determine the separate effect and role of surface and internal nucleation on the peak height and temperature of a DTA crystallization exotherm.*

C. MEETINGS ATTENDED

1. 96th Annual meeting of the American Ceramic Society, Indianapolis, IN, 24-28 April, 1994.
2. Microgravity Materials Science Conference, Huntsville, AL, 24-25 May, 1994.

D. PRESENTATION/PUBLICATION

1. Heterogeneous Nucleation in Lithium Disilicate Glass: L. Narayan, T. C. Cull, K. F. Kelton and C. S. Ray, 96th Annual Meeting of the American Ceramic Society, 24-28 April, 1994, Indianapolis, IN (Paper# G-71-94).
2. Nucleation Rate Curve for a $Li_2O.2SiO_2$ Glass by Dielectric Measurements: W. Huang and C. S. Ray, 96th Annual Meeting of the American Ceramic Society, 24-28 April, 1994, Indianapolis, IN (Paper# SVI-56-94).

A paper summarizing the results obtained to-date for the work under the present contract (Kinetics of Phase Transformation in Glass Forming Systems, Contract: NAG8-898) was presented at the Microgravity Materials Science Conference in Huntsville, AL, 24-25 May, 1994. A copy of this paper which was submitted at the conference, is enclosed.

DISTRIBUTION

1. Dr. Edwin C. Ethridge ES 74 George C. Marshall Space Flight Center National Aeronautics and Space Administration Huntsville, AL 35812.	3
2. NASA Science and Technical Information Facility P O Box 8757 Baltimore/Washington International Airport Baltimore, MD 21240.	2

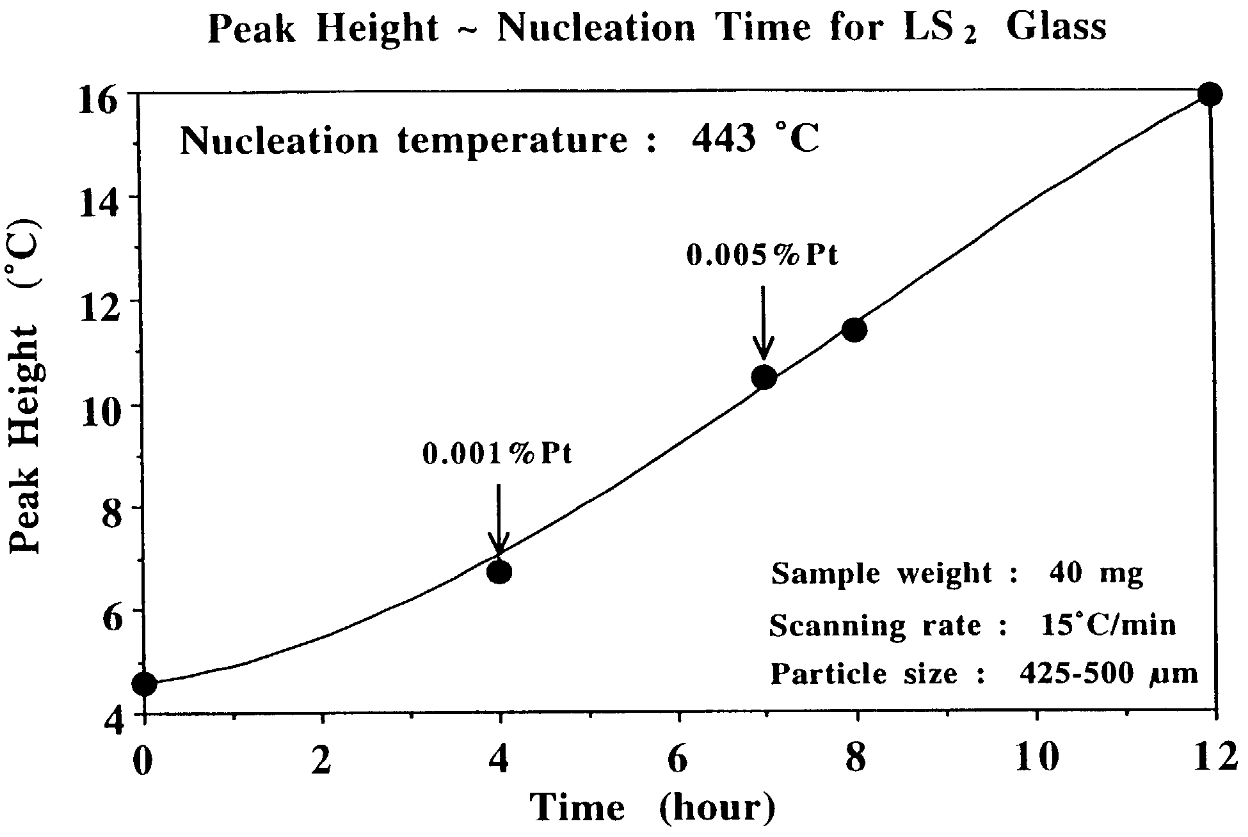

Fig 1. The maximum height of the DTA crystallization peak for an undoped lithium disilicate glass (solid circles) prenucleated isothermally at 443°C for different times. The arrows in the figure correspond to the peak heights for as-quenched lithium disilicate glass doped with 0.001 and 0.005 wt% platinum.

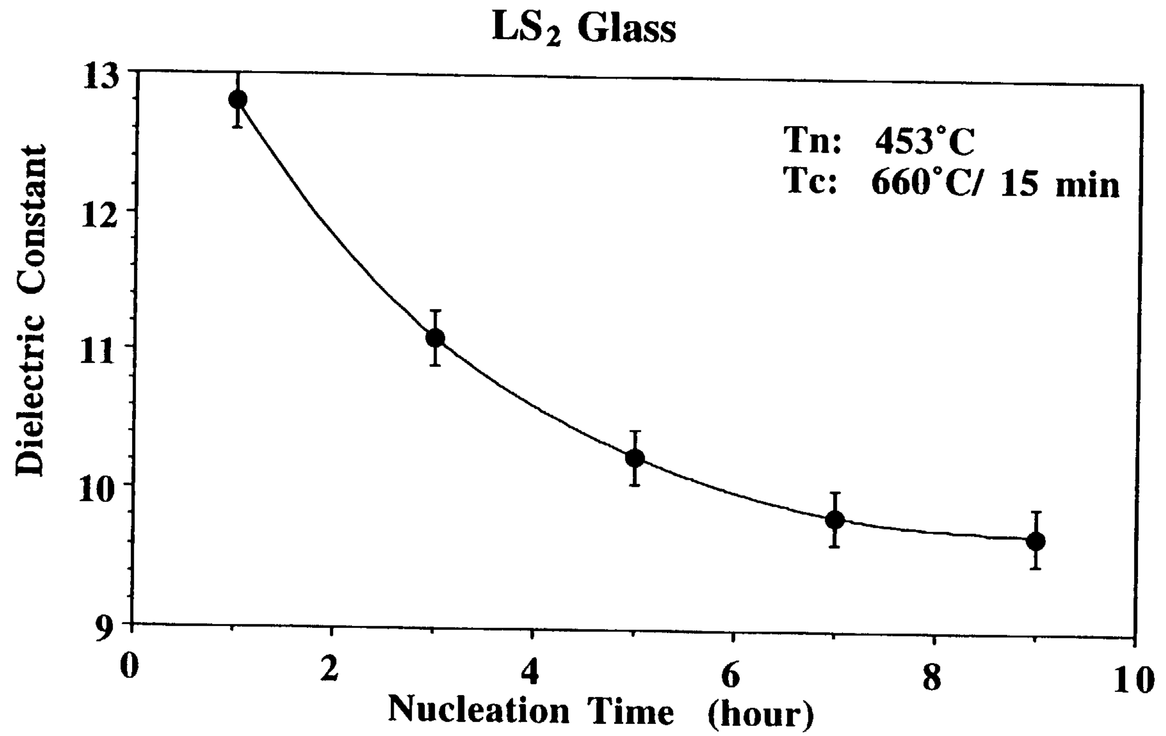

Fig 2. The dielectric constant at 1 kHz for lithium disilicate glass-ceramics prepared by nucleating at 453°C for different times shown and crystallizing at 660°C for 15 min. Sample size: ~ 8 mm diameter, 1 mm thick.

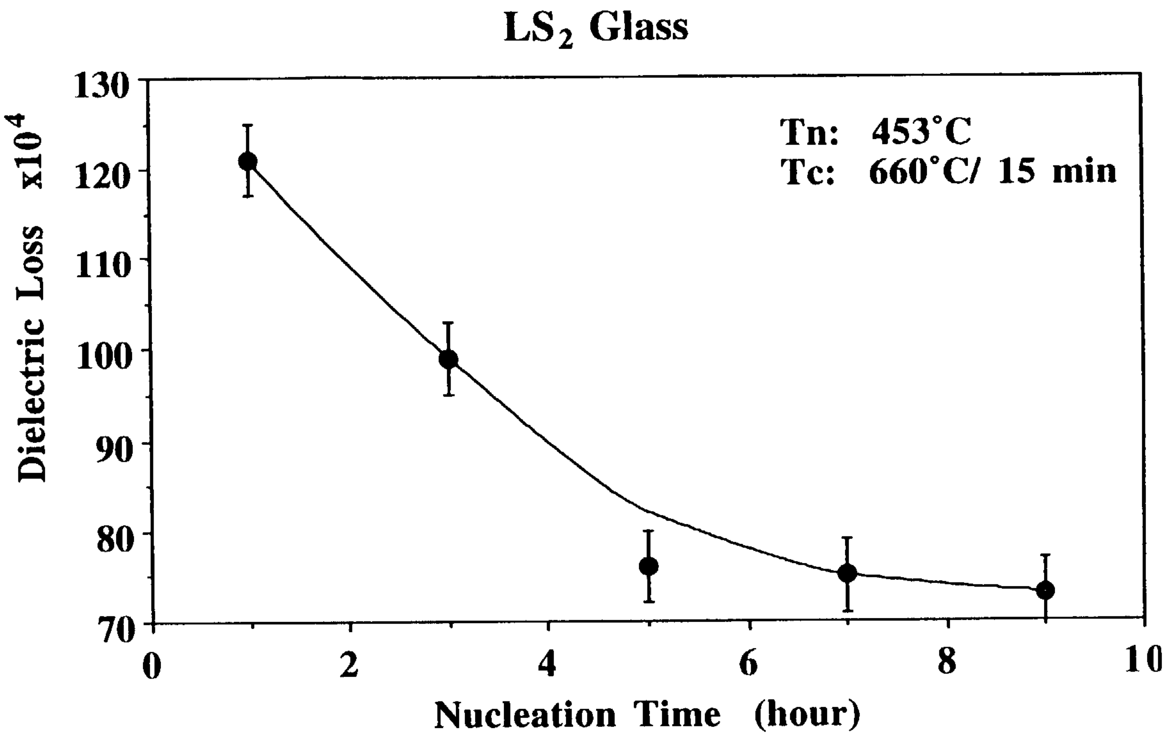

Fig 3. The loss factor at 1 kHz for lithium disilicate glass-ceramics prepared by nucleating at 453°C for different times shown and crystallizing at 660°C for 15 min. Sample size: ~ 8 mm diameter, 1 mm thick.

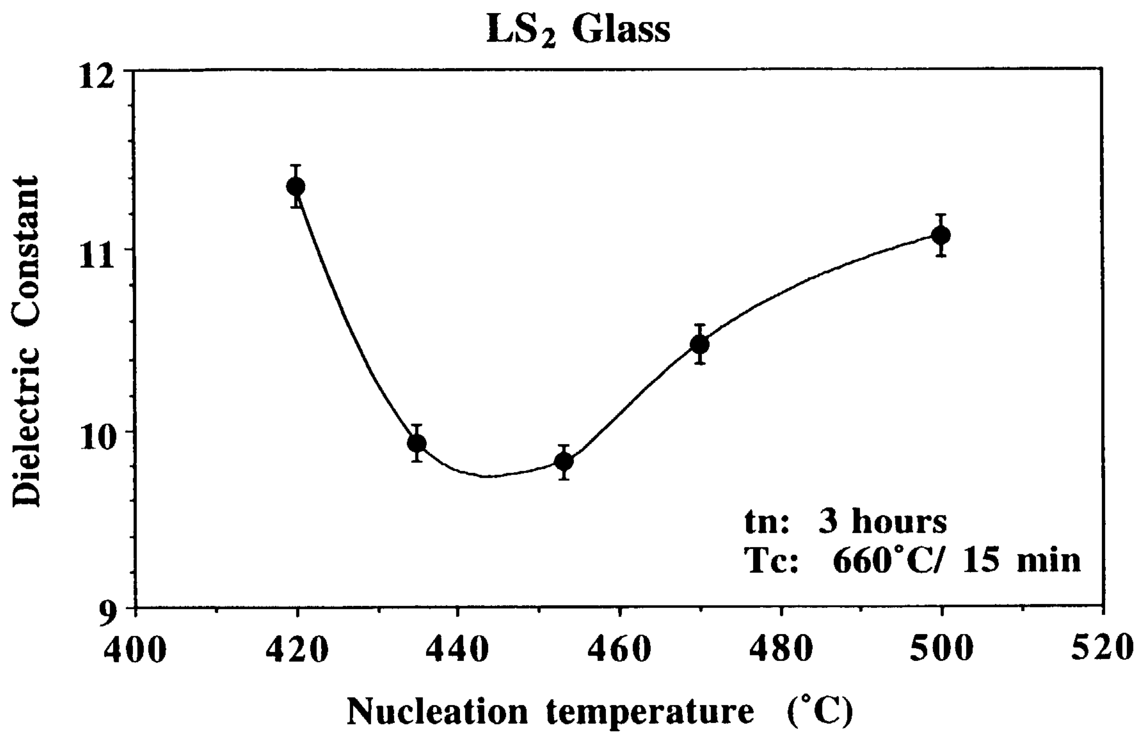

Fig 4. The dielectric constant at 1 kHz for lithium disilicate glass-ceramics prepared by nucleating at different temperatures shown for 3 h and crystallizing at 660°C for 15 min. Sample size: ~ 8 mm diameter, 1 mm thick.

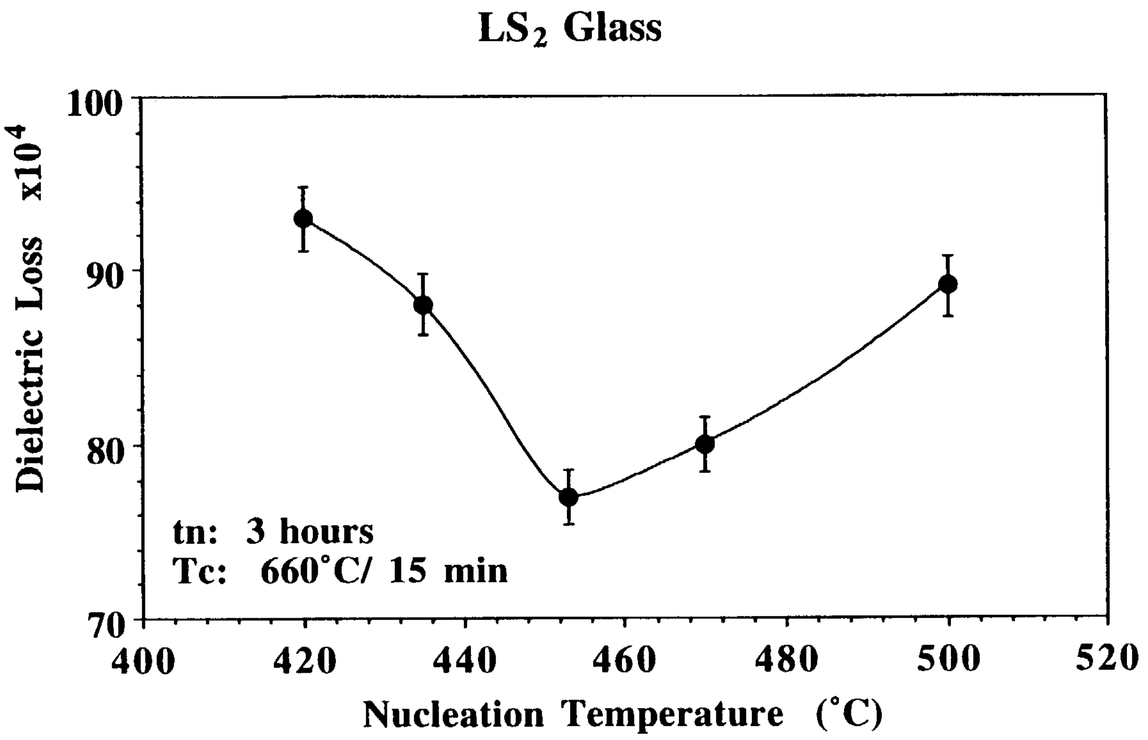

Fig 5. The loss factor at 1 kHz for lithium disilicate glass-ceramics prepared by nucleating at different temperatures shown for 3 h and crystallizing at 660°C for 15 min. Sample size: ~ 8 mm diameter, 1 mm thick.

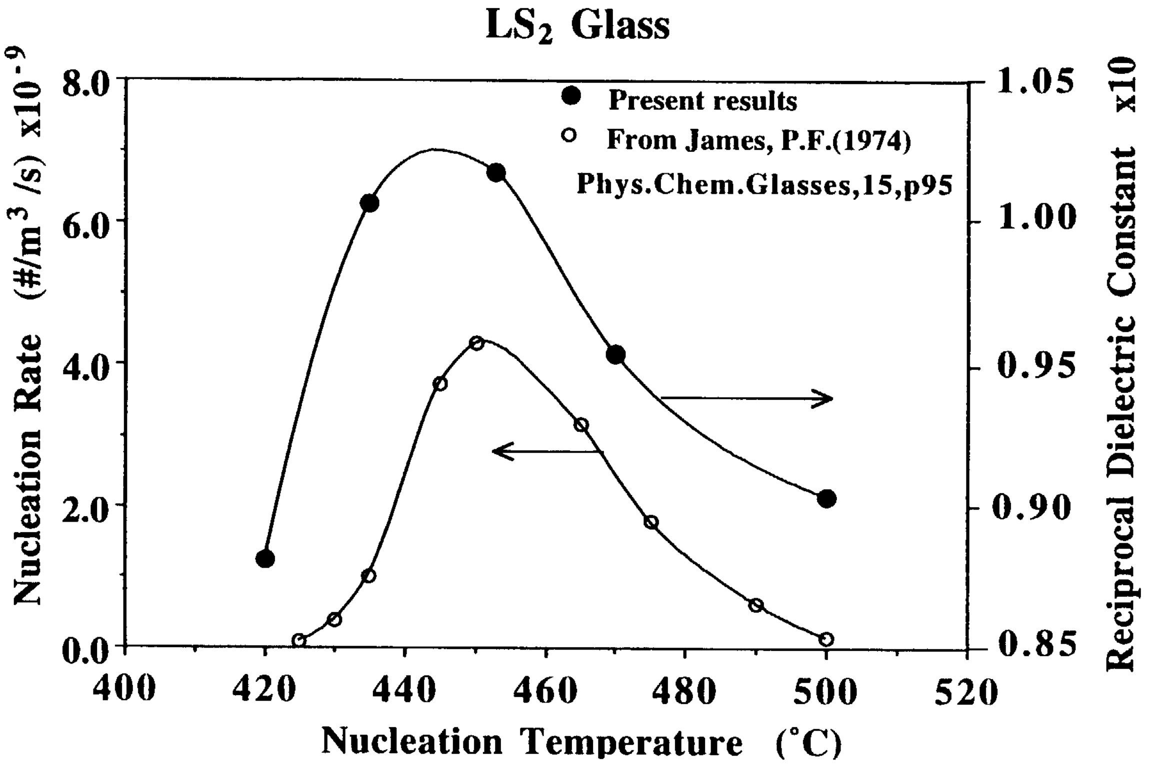

Fig 6. The reciprocal dielectric constant (solid circles) at 1 kHz for lithium disilicate glass-ceramics prepared by nucleating at different temperatures shown for 3 h and crystallizing at 660°C for 15 min (Sample size: ~ 8 mm diameter, 1 mm thick). The shape of this curve closely resembles the shape of the nucleation rate curve for the lithium disilicate glass and yields the temperature for maximum nucleation at ~ 445°C and a temperature range for nucleation from 420 to 500°C. For comparison, the nucleation rate curve for this glass determined by traditional method has also been included in this figure (open circles), which yields the temperature for maximum nucleation at ~ 453°C and a temperature range for nucleation from 425 to 500°C.