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Identifying internal and surface crystallization by differential thermal analysis for the glass-to-crystal transformations[1]

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Abstract

A differential thermal analysis (DTA) method has been developed that identifies and distinguishes surface and internal (bulk) crystallization that occurs during the crystallization of a glass. This method is rapid, convenient and requires only a few (about 6–8) DTA experiments to identify the dominant crystallization mechanism (bulk vs. surface) in the glass. In this method, either the maximum height of the DTA crystallization peak, $(\delta T)_p$, or the ratio $T_p^2/(\Delta T)_p$ where T_p is the temperature at $(\delta T)_p$ and $(\Delta T)_p$ is the peak half-width, is determined as a function of size of the glass particles used for the DTA measurements.

When analyzed by this technique, an as-quenched lithium disilicate (LS_2) glass was found to crystallize predominantly by surface crystallization. The tendency for surface crystallization was enhanced when the glass particles were exposed to moisture prior to DTA. Internal or bulk crystallization dominated over surface crystallization when this LS_2 glass was doped with small amounts of platinum.

The DTA curves in the literature for several soda–lime–silica glasses as a function of particle size were analyzed by the present method. The analysis showed that $Na_2O.CaO.2SiO_2$ and $Na_2O.2CaO.3SiO_2$ glasses crystallized by internal crystallization, but surface crystallization was the dominant crystallization mechanism for an $Na_2O.CaO.3SiO_2$ glass. These results agree with those obtained from an analysis of the apparent activation energy for crystallization as a function of particle size for these glasses.

Keywords: Crystallization; DTA; Glass; Mechanism; Transformation

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[1] Dedicated to Professor Hiroshi Suga.

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1. Introduction

The overall crystallization process that occurs in glasses during reheating is a complex structural reorganization that is hard to classify uniquely into the so-called internal (bulk) or surface mechanisms. In most glasses, crystallization by internal and surface mechanisms proceeds simultaneously and competitively. The kinetic and thermodynamic properties, such as the diffusion coefficient, difference in free energy (per unit volume) and interfacial energy between the crystalline and glassy phases, molar volume, and the entropy of fusion, all of which depend upon the glass composition, generally determine which specific mechanism would dominate the crystallization of a particular glass [1–3]. Knowledge of the dominant crystallization mechanism for the glass-to-crystal transformation has both scientific and technological value. For example, in developing glass-ceramics with desirable microstructure and properties, prior knowledge of the crystallization mechanism is useful in selecting the appropriate temperature–time processing conditions. For glasses having a strong tendency to crystallize internally, the controlled nucleation and crystallization of the glasses in bulk form is the desirable route to prepare glass-ceramics [4]. Glasses where surface crystallization is dominant are cerammed by sintering glass particles at a suitable temperature and pressure [4]. To prepare tape-cast, screen-printed, piezoelectric or pyroelectric glass-ceramics, a base glass which crystallizes by a surface mechanism is highly desirable [5].

This paper describes an experimental method that can rapidly and conveniently determine whether a glass crystallizes primarily by surface or bulk crystallization. In the present technique, which uses differential thermal analysis (DTA), the maximum height or half-width of the DTA crystallization peak is measured as a function of the particle size of the glass sample, while using a constant DTA heating rate for all the measurements. An $Li_2O.2SiO_2(LS_2)$ glass was used primarily in the present investigation. The tendency for internal crystallization was increased and its effect investigated using glasses containing small amounts of platinum which functioned as a nucleating agent. Likewise, the surface nucleation sites were increased by deliberately exposing the glass particles to a moist atmosphere prior to the DTA measurements. The applicability of the present technique was verified using the DTA curves reported [6–8] previously for the Na_2O–CaO–SiO_2 glasses. The theoretical justification of this experimental method for differentiating internal and surface crystallization is currently under study.

2. Experimental procedure

A well-mixed, 50 g batch of the $Li_2O.2SiO_2$ (LS_2) composition was melted in a platinum crucible at 1475°C for 3 h (air atmosphere) and then cast between two steel plates. Before casting, the melt was stirred periodically (30–40 min intervals) with a silica rod to ensure homogenization of the glass. X-ray diffraction (XRD) and examination by scanning electron microscopy (SEM) showed no evidence of unmelted or crystalline particles in the as-quenched glass. The silica content of the glass was determined by measuring the intensity (counts per s) of the Si- Kα peak for the glass by energy-dispersive X-ray analysis (EDAX) and comparing it with that of a silica standard for an identical beam current and scan area. Based on 12 different locations, each $\sim 0.1 \times 0.1\,\mathrm{mm}^2$ area, the average silica content of the glass was within ± 1.5 wt% of that in the batch. The quenched glass was ground and screened to five different particle sizes: 0.025–0.045, 0.075–0.106, 0.180–0.300, 0.425–0.500, and 0.850–1.190 mm, which were stored in a vacuum desiccator until used for DTA measurements. For analyzing the experimental results as a function of glass particle size, each of the five different ranges of particle size was represented by the numbers 0.035, 0.090, 0.240, 0.462, and 1.020 mm, which are close to the average for each size range.

The effect of particle size on the DTA peak profile for the LS_2 glass was investigated by heating glass particles of different size in the DTA apparatus at $15^\circ\mathrm{C\,min}^{-1}$ from room temperature until crystallization was complete. Platinum containers were used for both the glass and reference (alumina) samples and a flowing nitrogen atmosphere of $\sim 50\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ was maintained during the DTA measurements. The DTA machine was calibrated periodically using In, Zn, and Al standards at the same conditions used for the sample measurements. The data were recorded and analyzed in a computer interfaced with the DTA machine. Except for the platinum-containing glasses, the weight of the glass samples was held constant at 40 mg. The samples used for DTA were as-quenched glass and received no pre-nucleation treatment.

To enhance the effect of surface crystallization, surface nucleation sites were deliberately created by exposing the glass particles to moist air at 100% relative humidity for 80 h before they were used for the DTA measurements (wet samples). Three different particle sizes, namely 0.035, 0.090, 0.462 mm, were used for this investigation. The same-sized glass particles were also kept in an oven at 120°C for the same 80 h time (dry samples) and then crystallized in the DTA in order to compare the DTA results for dry and wet glass particles.

Since the tendency for internal crystallization is expected to increase when heterogeneous nuclei are uniformly distributed throughout the glass, DTA measurements were repeated for LS_2 glasses containing 0.001 and 0.005 wt% platinum. The results were compared with those of the LS_2 base glass (free of platinum). The platinum-containing glasses were prepared by adding a $PtCl_4$ solution to the batch, melting the batch and quenching the melt in the same way as was done for the undoped LS_2 glass.

3. Results and discussion

3.1. $Li_2O.2SiO_2$ (LS_2) glass (undoped)

The decrease in the maximum height of the DTA crystallization peak $(\delta T)_p$ measured at $15^\circ\mathrm{C\,min}^{-1}$ for 40 mg of as-quenched LS_2 glass, which occurred with increasing glass particle size, is shown in Fig. 1. The ratio of the total effective surface area to the total volume for a fixed weight of glass decreases with increasing particle size. Consequently, the number of active surface nuclei and, hence, the heat generated from the surface crystallization decrease as the particle size of the glass increases. The

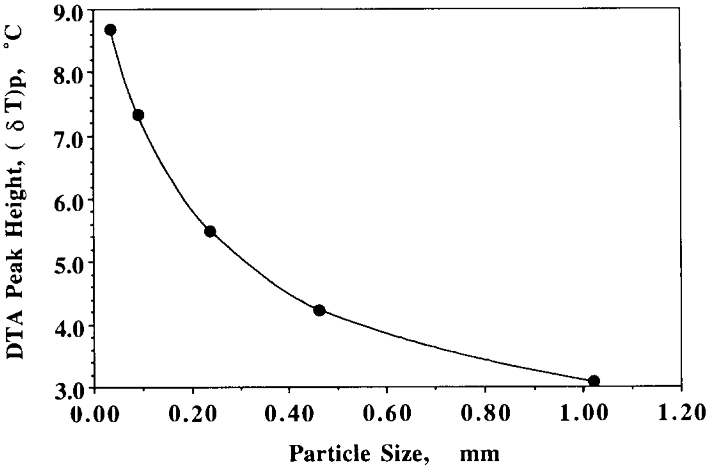

Fig. 1. The maximum height of the DTA crystallization peak $(\delta T)_p$ for lithium disilicate glass as a function of particle size. Sample weight: 40 mg. DTA heating rate: 15 °C min^{-1}.

decrease in $(\delta T)_p$ observed with increasing particle size, therefore, indicates that an as-quenched LS_2 glass crystallizes primarily by surface crystallization. Had bulk (internal) crystallization been the dominant mechanism for the crystallization of this glass, $(\delta T)_p$ would have increased rather than decreased with increasing particle size.

The $(\delta T)_p$ for 40 mg of the dry and wet LS_2 glasses is compared in Fig. 2 as a function of particle size. Clearly, the effect of surface crystallization on $(\delta T)_p$ is larger in the wet

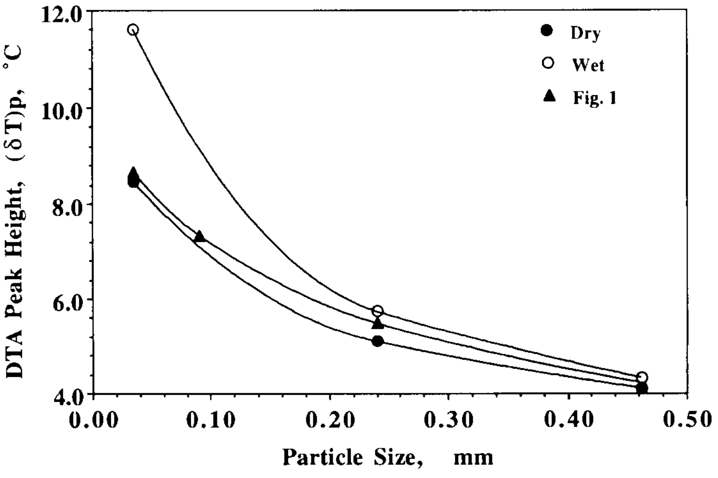

Fig. 2. Dependence of maximum height of the DTA crystallization peak $(\delta T)_p$ on particle size for lithium disilicate glass under different conditions of storing the glasses prior to DTA. The glass particles were stored in a vacuum desiccator (desiccated, shown in Fig. 1), in an oven at 120 °C for 80 h (dry), or in moist air at 100% relative humidity for 80 h (wet). Sample weight: 40 mg. DTA heating rate: 15 °C min^{-1}.

samples than that in the dry samples. The difference in $(\delta T)_p$ between the wet and dry samples is more pronounced for the smaller particles, where the total effective surface area is larger, than for the larger particles. The decrease in $(\delta T)_p$ with increasing particle size even for the dry samples confirms that surface crystallization is the dominant mechanism in the crystallization process of this lithium disilicate glass. Also compared in Fig. 2 (solid triangles) is the dependence of $(\delta T)_p$ on particle size shown in Fig. 1 for the glass stored in a vacuum desiccator. This comparison shows that the curve for the glass stored in the vacuum desiccator is very close to that for the dry glass, which suggests that storing in a vacuum desiccator keeps this glass reasonably dry. However, the slightly larger $(\delta T)_p$ values for the samples stored in the vacuum desiccator, compared to the samples dried at 120°C for 80 h, suggest a slight moisture attack occurred on the particles in the vacuum desiccator.

The temperature corresponding to the maximum of the DTA crystallization peak, T_p, increased with increasing particle size, Fig. 3, in an identical fashion for the wet, dry, or desiccated glass. This increase in T_p indicates that crystallization becomes increasingly difficult with increasing particle size. Except for the smallest 0.035 mm particles of the wet glass, the T_p for the dry, wet, and desiccated glasses was almost indistinguishable at any particle size. The T_p for the 0.035 mm wet particles was about 8°C lower than that of the dry and desiccated particles. As indicated by the peak height plot in Fig. 2, the wet glass contains a higher number of surface nuclei, especially for the smaller particle sizes, which makes these particles easier to crystallize. So, the observed lower value of T_p for the 0.035 mm wet particles compared to that for the dry and desiccated particles is expected.

The crystal growth dimension n (also known as Avrami parameter), given by [9]

$$n = [2.5/(\Delta T)_p]/(E/RT_p^2) \tag{1}$$

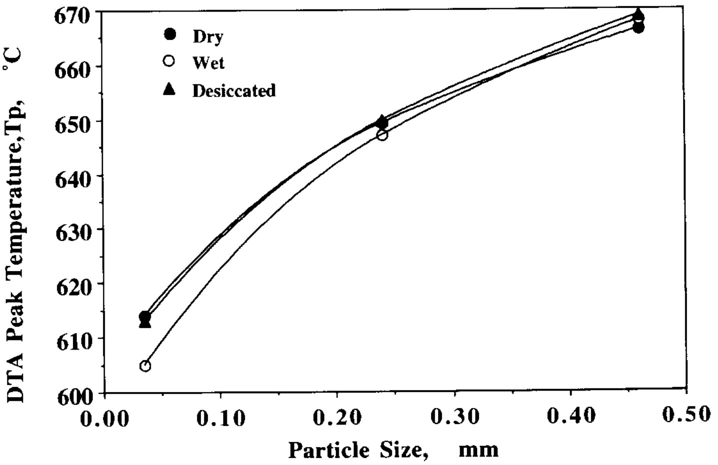

Fig. 3. The temperature at the maximum height of the DTA crystallization peak T_p for lithium disilicate glass particles which have been stored at different conditions prior to DTA. For conditions of experiments and of storing the glass particles, see Fig. 2.

is frequently used to describe surface or internal crystallization. A value of n close to 3 signifies internal or three-dimensional crystallization and a value close to 1 indicates surface crystallization. Intermediate values of n between 1 and 3 are indicative of both surface and internal crystallization. In Eq. (1), $(\Delta T)_p$ is the width of the DTA peak at half-maxima (half-width), R is the gas constant, and E is the activation energy for crystal growth. If E is assumed to be independent of particle size, $[T_p^2/(\Delta T)_p]$ would be proportional to n and plotting it as a function of particle size could give a qualitative idea for the dominant crystallization mechanism in the glass.

The plot of $[T_p^2/(\Delta T)_p]$ as a function of particle size is shown in Fig. 4 for the dry, wet, and desiccated LS_2 glass particles. These curves show a dependence on the particle size similar to that in Fig. 2 for $(\delta T)_p$, i.e. $[T_p^2/(\Delta T)_p]$ decreases with increasing particle size for all the glasses. If internal crystallization was the dominant mechanism, $[T_p^2/(\Delta T)_p]$ would increase with particle size ensuring, according to Eq. (1), an increase in the value for n. However, a decrease in $[T_p^2/(\Delta T)_p]$ with increasing particle size is also not quite reasonable even if surface crystallization was the dominant mechanism. For predominately surface crystallization, the values of $[T_p^2/(\Delta T)_p]$ for the dry, wet, and desiccated samples should ideally be the same, particularly for the smallest 0.035 mm particles, thereby, yielding a value of n close to 1 for all the samples at this particle size. If surface crystallization continues to be the primary mechanism and E does not change appreciably with particle size, $[T_p^2/(\Delta T)_p]$ for all the particle size samples should be nearly the same. In other words, the plot of $[T_p^2/(\Delta T)_p]$ as a function of particle size should be a straight line nearly parallel to the horizontal axis. The reason for the decrease in $[T_p^2/(\Delta T)_p]$ with increasing particle size is not clear at this time. Despite this unexplained feature the curves in Fig. 4 demonstrate that it is not internal but rather surface crystallization which dominates the crystallization process of the lithium disilicate glass.

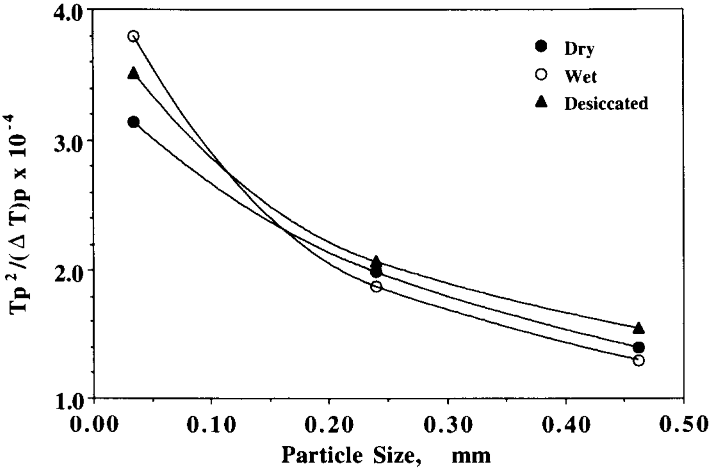

Fig. 4. The ratio of the square of the peak temperature T_p to peak half-width $(\Delta T)_p$ as a function of particle size for lithium disilicate glass particles stored under different conditions prior to DTA. For conditions of experiments and of storing the glass particles, see Fig. 2.

3.2. LS_2 glass doped with platinum

To further verify whether surface crystallization is the dominant mechanism for the crystallization of undoped LS_2 glass, identical DTA measurements were repeated for LS_2 glasses containing 0.001 and 0.005 wt% platinum as a heterogeneous nucleating agent. The results were compared with those for the undoped LS_2 base glass. Platinum-nucleated glasses are expected to crystallize primarily by bulk or internal crystallization. Since the platinum-nucleated glasses yield such a large DTA peak height that the temperature of the DTA furnace becomes unstable, 40 mg of sample, as was used for the undoped base glass, could not be used for these measurements. A 40 mg sample of LS_2 glass composed of 0.462 mm average size particles and containing 0.005 wt% Pt yields a peak whose height is 40°C larger than that of the base glass, at a scanning rate of 15°C min^{-1}. The weight of the platinum-containing glasses was adjusted according to their platinum content so that the DTA peak height did not exceed 8–10°C when 0.462 mm glass particles was scanned at 15°C min^{-1}. This weight of glass was then held constant for the measurements on other particle sizes (about 15 mg for the 0.005 wt% and 20 mg for the 0.001 wt% Pt-containing glasses).

Since the weight of glass was different for different samples, a direct comparison of $(\delta T)_p$ for these glasses was difficult. A new term, "reduced peak height", which maintains the same functional trend as the original peak height with particle size but makes a direct comparison possible, was defined as

$$\text{Reduced } (\delta T)_p = [(\delta T)_p \text{ for a particular particle size}]/[(\delta T)_p \text{ for the smallest particle size, 0.035 mm in this case}]$$

The reduced $(\delta T)_p$ for the undoped LS_2 glass and those containing 0.001 and 0.005 wt% Pt are compared in Fig. 5 as a function of particle size. The shape of the curves in Fig. 5 clearly demonstrates that internal or bulk crystallization dominates in the platinum-containing glasses, especially, the glass containing 0.005 wt% Pt where the reduced $(\delta T)_p$ increases with increasing particle size as opposed to the decrease observed for the undoped base glass. For the glass containing 0.001 wt% Pt, the reduced $(\delta T)_p$ decreases just slightly with increasing particle size. In this case, as the particle size increases the decrease in $(\delta T)_p$ caused by the decrease in surface crystallization (less surface area) is nearly counterbalanced by the increase in $(\delta T)_p$ caused by increasing internal crystallization (more heterogeneous nuclei).

As was observed for dry and wet undoped glasses, T_p for the platinum-containing glasses also increased with increasing particle size, compare Fig. 3 with Fig. 6. It is also clear from Fig. 6 that T_p decreases with increasing concentration of platinum in the glass for any particle size. This reduction is expected since it suggests that crystallization becomes more favorable with increasing platinum content in the glass. However, unlike $(\delta T)_p$, T_p for a glass always increases with increasing particle size, no matter whether the glass is doped, undoped, wet, or dry. When compared with a glass of identical composition and particle size, the measured T_p can only predict which glass contains a higher concentration of nuclei. The dependence of T_p on particle size,

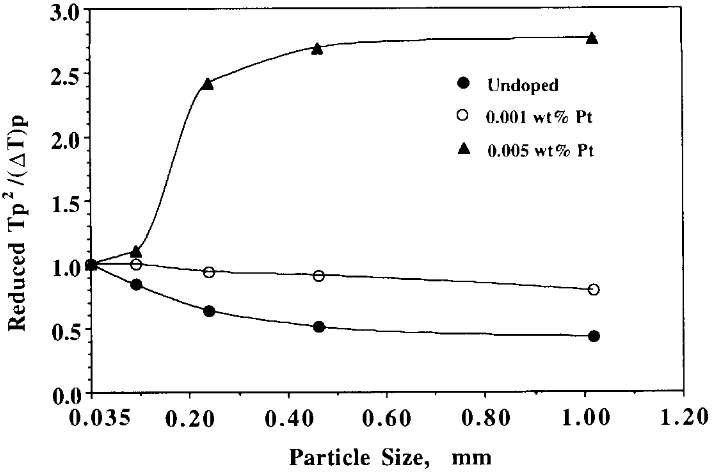

Fig. 5. Reduced maximum DTA peak height $(\delta T)_p$ as a function of particle size for undoped and platinum-containing lithium disilicate glasses. See text for the definition of reduced peak height. Sample weight: 40 mg (undoped glass), 20 mg (glass containing 0.001 wt% Pt), 15 mg (glass containing 0.005 wt% Pt). DTA heating rate: 15 °C min^{-1}.

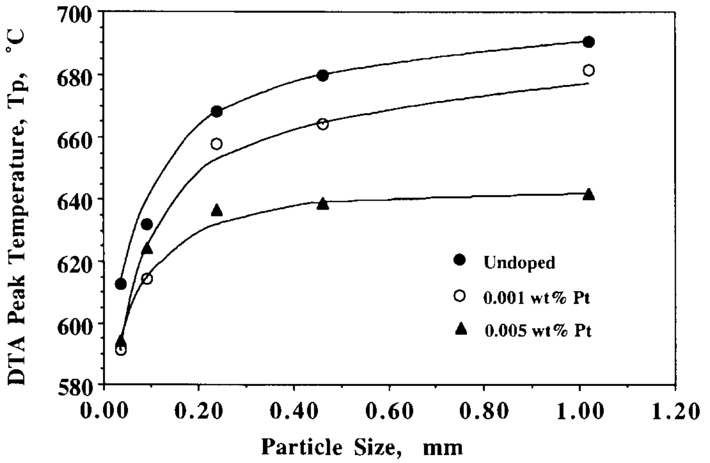

Fig. 6. Temperature of the DTA peak maximum T_p as a function of particle size for undoped and platinum-containing lithium disilicate glasses. Sample weight and DTA heating rate are the same as those given in Fig. 5.

therefore, cannot provide information for the crystallization mechanism (surface and/or internal) that occurs when these glasses crystallize.

As mentioned previously, the dependence of $[T_p^2/(\Delta T)_p]$ on particle size may closely resemble the dependence of the crystal growth dimension n of the glass. Values of $[T_p^2/(\Delta T)_p]$ for the platinum-containing glasses were calculated from the measured T_p

and $(\Delta T)_p$ and reduced, for a better comparison, in the same way as was done for $(\delta T)_p$, i.e.

$$\text{Reduced } [T_p^2/(\Delta T)_p] = [T_p^2/(\Delta T)_p] \text{ for any particle size}/[T_p^2/(\Delta T)_p] \text{ for the smallest particle size, 0.035 mm in this case}$$

Fig. 7 shows that the plots of reduced $[T_p^2/(\Delta T)_p]$ as a function of particle size for the doped and undoped LS_2 glasses closely resemble the plots in Fig. 5 of the reduced $(\delta T)_p$ as a function of particle size for these glasses. Thus, like reduced $(\delta T)_p$, reduced $[T_p^2/(\Delta T)_p]$ also provides the same information, namely, surface crystallization dominates in the undoped LS_2 glass. When doped with platinum, bulk crystallization becomes the dominant mechanism in this glass, as indicated by an increase in $[T_p^2/(\Delta T)_p]$ or the growth dimension *n*, see Eq. (1), with increasing particle size.

3.3. $Na_2O.CaO.2SiO_2$ (NCS_2, $Na_2O.CaO.3SiO_2$ (NCS_3), and $Na_2O.2CaO.3SiO_2$ (NC_2S_3) glasses

The reduced $(\delta T)_p$ and reduced $[T_p^2/(\Delta T)_p]$ curves for the NCS_2, NCS_3, and NC_2S_3 glasses, calculated from the DTA thermograms reported previously by others [6,7] and ourselves [8], are shown in Figs. 8 and 9 as a function of particle size. As was observed for the LS_2 glasses, the plots of $(\delta T)_p$ for these three glasses as a function of particle size resemble the plots of $[T_p^2/(\Delta T)_p]$, compare Figs. 8 and 9. Both $(\delta T)_p$ and $[T_p^2/(\Delta T)_p]$ decrease for the NCS_3 glass and increase for the NC_2S_3 glass as the particle size increases. For the NC_2S_3 glass, only two data points were

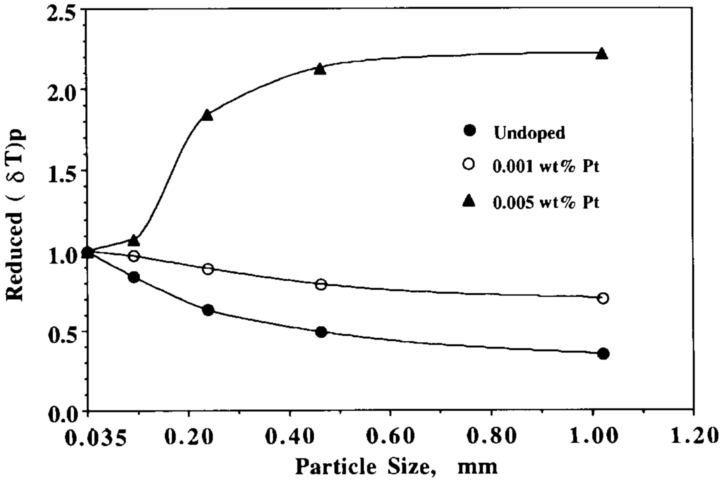

Fig. 7. Reduced ratio of the square of the DTA peak temperature T_p to peak half-width $(\Delta T)_p$ as a function of particle size for undoped and platinum-containing lithium disilicate glasses. Sample weight and DTA heating rate are the same as those given in Fig. 5.

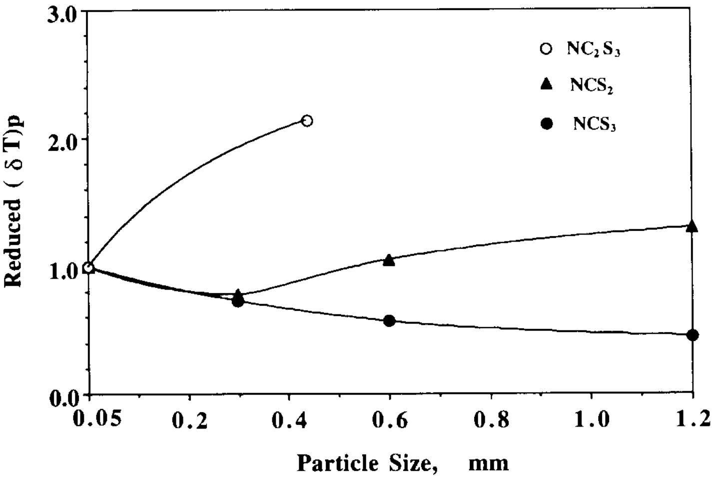

Fig. 8. Reduced maximum DTA peak height $(\delta T)_p$ as a function of particle size for $Na_2O.2CaO.3SiO_2$ (NC_2S_3), $Na_2O.CaO.2SiO_2$ (NCS_2) and $Na_2O.CaO.3SiO_2$ (NCS_3) glasses. For these plots, the DTA curves of NCS_2 and NCS_3 glasses in Ref. [6], and NC_2S_3 glass in Ref. [8] were used. Sample weight: 200 mg for NCS_2 and NCS_3 glasses, 30 mg for NC_2S_3 glass. DTA heating rate: 10 °C min^{-1}.

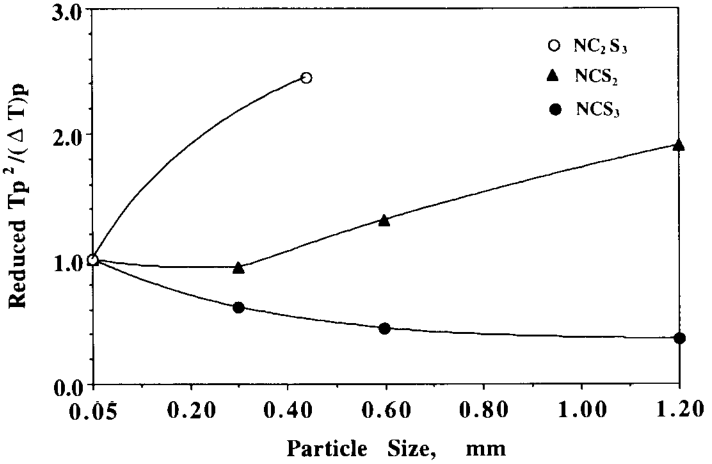

Fig. 9. Reduced ratio of the square of the DTA peak temperature T_p to the peak half-width $(\Delta T)_p$ as a function of particle size for NC_2S_3, NCS_2, and NCS_3 glasses. The DTA curves of NCS_2 and NCS_3 glasses in Ref. [6], and NC_2S_3 glass in Ref. [8] were used to generate these plots. For sample weight and DTA heating rate, see Fig. 8.

available for analysis, but the increase in either $(\delta T)_p$ or $[T_p^2/(\Delta T)_p]$ with increasing particle size is clearly evident. For the NCS_2 glass, $(\delta T)_p$ or $[T_p^2/(\Delta T)_p]$ decreases initially with increasing particle size, and then increases as the particle size exceeds about 0.3 mm.

Based on our interpretation for the LS_2 glasses, the curves in Figs. 8 and 9 indicate that the NCS_3 and NC_2S_3 glasses crystallize primarily by surface and internal crystallization, respectively. The NCS_2 glass crystallizes primarily by internal crystallization, although surface crystallization appears to be dominant for smaller particle sizes. The conclusion for the crystallization processes of NCS_2, NCS_3, and NC_2S_3 glasses made from the DTA data analysis techniques used in the present investigation agrees with that reported previously [6–8] from an analysis of apparent activation energy for crystallization of these glasses as a function of particle size.

4. Conclusions

A DTA method has been developed that identifies and distinguishes surface from internal crystallization processes in glasses. This technique which requires only a small quantity of glass and a few DTA scans using glass particles of different size, is a rapid and convenient method of determining whether a glass crystallizes primarily by surface or internal crystallization. No special sample preparation technique involving cutting, grinding, polishing, or etching is required. There is no other convenient and less time-consuming method known to date, which can provide information for the dominant crystallization mechanism in a glass.

It has been shown in the present investigation that a lithium disilicate (LS_2) glass crystallizes primarily by surface crystallization as opposed to the general belief [10, 11] that homogeneous nucleation leading to internal (or bulk) crystallization occurs in an undoped LS_2 glass. The theoretical justification of the present technique in identifying surface from internal crystallization is currently under investigation. Preliminary results [12] show that the DTA curves for the LS_2 glass generated by computer modeling represent the experimental curves more closely when surface crystallization is assumed to be dominant over internal crystallization. The present method successfully demonstrates the enhancement of surface crystallization when the LS_2 glass particles are exposed to moisture prior to crystallization. Likewise, the internal crystallization becomes clearly evident when this glass is doped with small amounts of platinum that provide heterogeneous nucleation sites inside the glass.

When DTA curves in the literature for $Na_2O.CaO.2SiO_2$ (NCS_2), $Na_2O.CaO.3SiO_2$ (NCS_3), and $Na_2O.2CaO.3SiO_2$ (NC_2S_3) glasses were analyzed by the present technique, the NCS_2 and NC_2S_3 glasses were found to crystallize primarily by internal crystallization, whereas surface crystallization was dominant in the NCS_3 glass. These results agreed with those determined from an analysis of the apparent activation energy for crystallization of these glasses as a function of particle size.

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