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A generalized method for determining the crystal nucleation and growth rates in glasses by differential thermal analysis

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A generalized experimental method that uses differential thermal analysis (DTA) has been developed for determining the nucleation rate (I), the crystal growth rate (U), and the concentration of quenched-in nuclei (N_q) in glasses. The method is applicable even for glasses, whose I and U curves (as a function of temperature) overlap to a considerable degree. Measuring I by the conventional method may yield an overestimated value for I if the chosen crystal growth temperature is within the region of overlap between I and U. When applied to a $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass, whose I and U curves are known to overlap considerably, the present DTA method yields values for I, U, and N_q that are in excellent agreement with the same values determined by the conventional methods.

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1. Introduction

Determining the rates of nucleation (I) and crystal growth (U) as a function of temperature, and the concentration of quenched-in-nuclei (N_q) in glasses is important to understanding the stability of glasses in practical applications as well as to developing glass-ceramic materials with desired micro structure and properties.

In the conventional method [1–10] of measuring I and U the glass samples are generally given a two-stage isothermal heat treatment; one to form nuclei in the glass (nucleation heat treatment at T_N) and the other at a higher temperature to grow those nuclei to observable size (crystal growth heat treatment at T_G). The values of I or U are determined by measuring the number (per unit volume) or size of the crystals on a polished and lightly etched surface of the heat treated samples via an optical microscope. For measuring I as a function of temperature, heat treatments at several T_N's for different times at each T_N are needed, keeping the crystal growth temperature and time constant. Similarly, isothermal heat treatments at several T_G for different times at each T_G are required for measuring U as a function of temperature. Although it is direct and straight forward, measuring I and U by conventional method appears time consuming and laborious.

A novel and unique experimental method which uses differential thermal analysis (DTA) was developed by Ray *et al.* [11] for rapidly determining I, U and N_q in glasses. This DTA method is much faster and requires a smaller amount of sample than the conventional method of measuring I, U, and N_q while yielding values for these parameters in excellent agreement with those determined by conventional method. Unlike the conventional method, the DTA method does not require any special sample preparations like cutting, grinding, polishing and etching. The laborious task of counting the number or measuring the size of crystals is also avoided in the DTA method. A conservative estimate indicates that to obtain an equivalent amount of data, the DTA method requires only about 1/15th of the amount of sample and 7 to 10 times less time compared to the conventional method.

In the DTA method, a small amount of glass, typically 40 to 60 mg, having a relatively large particle size (>400 μm), been first given an isothermal nucleation heat treatment in the DTA apparatus at T_N for a time t_N and then a short crystal growth heat treatment at T_G for a time t_G. After this treatment, the sample is heated in the DTA apparatus at a relatively high heating rate, typically between 10 and 25°C/min. An exothermic DTA peak will be observed for crystallization of the glass that remained untransformed after the crystal growth heat treatment at T_G. The area of this DTA peak is proportional to the number of nuclei present in the untransformed glass. From the area of two such DTA peaks, where all the experimental parameters except the heat treatment time at T_G are constant, the values for I_N (at T_N) can be calculated from the following equation [11],

$$\frac{A_1}{A_2} = \frac{M_1\left[1 - \frac{\pi}{3}(I_N t_N + N_q)(U_G t_{G1})^3\right]}{M_2\left[1 - \frac{\pi}{3}(I_N t_N + N_q)(U_G t_{G2})^3\right]} \qquad (1)$$

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where, A_1 and A_2 are the area of the DTA peaks after crystal growth heat treatment at T_G for times t_{G1} and t_{G2}, respectively, and M_1 and M_2 are the sample mass for the two DTA runs. The quantity $(I_N t_N + N_q)$ is the total number of nuclei per unit volume of the glass, where $(I_N t_N)$ is the number of nuclei developed per unit volume due to the nucleation heat treatment only. A plot of $(I_N t_N + N_q)$ as a function of t_N yields a straight line, whose slope gives the value of I_N. By repeating the experiments at different T_N, the complete nucleation rate curve as a function of temperature can be determined. In using Equation 1, it is assumed that the value of U_G at T_G is known, which can be determined by the conventional method.

The concentration of quenched-in nuclei, N_q, can be calculated also using Equation 1 when the experiments are performed using an as-quenched glass, i.e., no nucleation treatment and $I_N t_N = 0$. Also, using the Equation 1, the crystal growth rate (U) at different temperatures can be determined from two DTA runs at each temperature using an as-quenched glass, see Ref. 11 for further experimental details.

The values of I and U determined at different temperatures for a lithium disilicate ($Li_2O \cdot 2SiO_2$ which is hereafter abbreviated as LS_2) glass using this DTA method [11] are in excellent agreement with the I and U values determined by the conventional method [1–4]. However, when applied to determine I, U, and N_q, in a soda-lime-silicate ($Na_2O \cdot 2CaO \cdot 3SiO_2$ hereafter abbreviated as NC_2S_3) glass, the DTA method appeared to yield erroneous results. An example is shown in Table I where the concentration of quenched-in nuclei, N_q, calculated using Equation 1 for different pairs of heat treatment times (t_G's) at T_G for the LS_2 and NC_2S_3 glasses are compared. The T_G for the LS_2 glass was 600°C and that for the NC_2S_3 glass was 670°C in the DTA experiments. As shown in Table I, the value of N_q for the LS_2 glass is independent of the pair of t_G's chosen, which is expected, since N_q is the number of nuclei formed during cooling the melt and, therefore, is a constant for the glass. The values of N_q for the NC_2S_3 glass varied significantly with the pair of t_G's used, which cannot be correct.

A likely reason for the inconsistent N_q values for the NC_2S_3 glass (Table I) may be the overlap of the I and U curves (as a function of temperature) for the glass. Additional nuclei may have formed during the crystal growth heat treatment. Equation 1 was derived with the assumption that the I and U curves are separated, which may be true for the LS_2 glass. For glasses where there is a considerable overlap of the I and U curves, crystal growth during the nucleation heat treatment and nucleation during the crystal growth heat treatment can occur simultaneously as shown schematically in Fig. 1. In this case, it will not be appropriate to use Equation 1 to determine I, U, or N_q from DTA data. It is important, therefore, to develop a generalized method by taking account of the effects of simultaneous nucleation and crystal growth so as to establish this unique DTA method as a widely acceptable means for rapidly determining the nucleation rate (I) and the crystal growth rate (U) as a function of temperature and the concentration of quenched-in nuclei in all types of glasses.

TABLE I Concentration of quenched-in nuclei, N_q, calculated using Equation 1 for LS_2 and NC_2S_3 glasses

t_{G1} (min)	t_{G2} (min)	N_q (m^{-3})-LS_2	N_q (m^{-3})-NC_2S_3
10	15	4.1×10^{12}	7.1×10^{13}
10	20	4.6×10^{12}	36.8×10^{13}
15	20	4.5×10^{12}	51.1×10^{13}

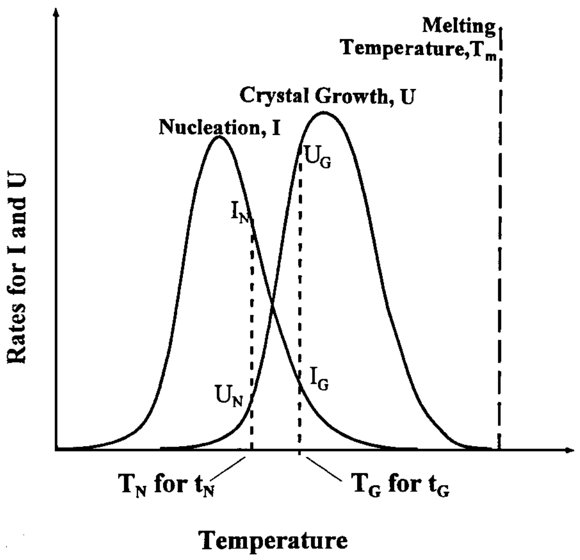

Figure 1 Schematic of nucleation (I) and crystal growth rate (U) curves for a glass.

A more generalized method than presented in Ref. 11 has been developed in the present work, where simultaneous nucleation and crystal growth at the heat treatment temperatures has been taken into account. As described in the next section, this modified method needs three additional DTA scans to determine first the values of N_q and the nucleation rate (I_G) at the crystal growth temperature. Once the values for N_q and I_G are known, the nucleation rate (I) or the crystal growth rate (U) at different temperatures can then be determined using procedures similar to that described in Ref. 11 i.e., using two DTA runs for determining I or U at each temperature.

2. Theoretical approach

As mentioned before, the DTA method of measuring the nucleation rate involves four general steps; (1) a nucleation heat treatment at T_N for a time t_N, (2) a crystal growth heat treatment at T_G for a time t_G, $T_G > T_N$, (3) reduce the temperature to a value well below the nucleation range and stabilize the sample at that temperature for about 5 min, and finally (4) perform a DTA scan at a fixed heating rate. When the I and U curves overlap as shown in Fig. 1, a portion of the glass will crystallize during the nucleation heat treatment at T_N and the volume fraction crystallized, V_{C1}, during nucleation at T_N for a time t_N can be given by,

$$V_{C_1} = V_0 \frac{\pi}{3}(I_N t_N + N_q)(U_N t_N)^3 \qquad (2)$$

where, V_0 is the initial volume of the glass sample, N_q is the concentration of quenched-in nuclei in the glass, I_N

and U_N are the steady state nucleation rate and crystal growth rate, respectively, at the nucleation temperature T_N, and the quantity, $(I_N t_N)$, is the number of nuclei formed per unit volume due to nucleation heat treatment. The volume of glass, V_{g1}, that remains untransformed after the nucleation treatment can be given by

$$V_{g_1} = V_0 - V_{C_1}$$

$$V_{g_1} = V_0\left[1 - \frac{\pi}{3}(I_N t_N + N_q)(U_N t_N)^3\right] \quad (3)$$

During the crystal growth heat treatment at T_G for a time t_G, an additional $(I_G t_G)$ number of nuclei will form per unit volume of the glass, where I_G is the steady state nucleation rate at T_G, and the volume fraction crystallized, V_{C2}, during crystal growth heat treatment can be written as

$$V_{C_2} = V_{g_1}\frac{\pi}{3}(I_N t_N + N_q + I_G t_G)(U_G t_G)^3$$

$$V_{C_2} = V_0\left[1 - \frac{\pi}{3}(I_N t_N + N_q)(U_N t_N)^3\right]\frac{\pi}{3}(I_N t_N + N_q + I_G t_G)(U_G t_G)^3 \quad (4)$$

where, U_G is the crystal growth rate at T_G.

In the final portion of the DTA run, an exothermic DTA peak will be produced by the crystal growth of the nuclei obtained in the volume of glass, V_{g2}, that still remained untransformed at the end of the crystal growth heat treatment. The area of this DTA peak, A, will be proportional to that number of nuclei, namely,

$$A = C V_{g_2}(I_N t_N + N_q + I_G t_G)$$

$$A = C(V_{g_1} - V_{C_2})(I_N t_N + N_q + I_G t_G) \quad (5)$$

where, C is a proportionality constant. In Equation 5, it was assumed that no new nuclei formed in the glass during the DTA scan, which can be accomplished if a high enough heating rate is used. Heating rates >8°C/min is usually sufficient to avoid additional nuclei formation, at least, in the NC_2S_3 glass.

Using Equations 3 for V_{g1} and 4 for V_{C2} in Equation 5, we get,

$$A = C V_0\left[1 - \frac{\pi}{3}(I_N t_N + N_q)\left(U_N^3 t_N^3\right)\right] \times\left[1 - \frac{\pi}{3}(I_N t_N + N_q + I_G t_G)\left(U_G^3 t_G^3\right)\right] \times (I_N t_N + N_q + I_G t_G) \quad (6)$$

V_0 in Equation 6 can be replaced by M/ρ where M is the mass of the sample used for the DTA experiment and ρ is the density of the glass. Expressing the peak areas, A_1 and A_2, for two DTA runs where all the experimental parameters except the time for crystal growth heat treatment at T_G are constant, by equations of the type given in Equation 6 and taking the ratio of A_1 and A_2, one obtains,

$$\frac{A_1}{A_2} = \frac{M_1\left[1 - \frac{\pi}{3}(I_N t_N + I_G t_{G1}) + N_q)U_G^3 t_{G1}^3\right][(I_N t_N + I_G t_{G1}) + N_q]}{M_2\left[1 - \frac{\pi}{3}(I_N t_N + I_G t_{G2}) + N_q)U_G^3 t_{G2}^3\right][(I_N t_N + I_G t_{G2}) + N_q]} \quad (7)$$

where, M_1 and M_2 are the sample mass, and t_{G1} and t_{G2} are the heat treatment times at T_G for the two DTA runs whose areas are A_1 and A_2, respectively. In the case of no overlap between I and U, I_G (at T_G) = 0 and Equation 7 reduces to Equation 1 as derived in Ref. 11. Equation 1, therefore, is only a special case of the more generalized form given by Equation 7.

As done previously [11] for measuring the nucleation rate, the number of nuclei $(I_N t_N)$ formed during the nucleation heat treatment at T_N will be determined as a function of t_N from two DTA measurements for each t_N. A plot of $(I_N t_N)$ vs. t_N should be a straight line whose slope yields the value of I_N at T_N. Determining $(I_N t_N)$ using Equation 7 requires three unknown parameters be known, namely, N_q, I_G, and U_G. As assumed previously [11], the value of U_G is assumed to be known also in the present investigation, which we recommend be determined by the conventional method. To determine N_q and I_G, three DTA runs for an as-quenched glass $(I_N t_N = 0)$ with different heat treatment times (t_{G1}, t_{G2}, t_{G3}) at T_G are required. If A_1, A_2, and A_3 are the respective DTA peak areas, then three equations of the following type can be developed for A_1/A_2, A_1/A_3, and A_2/A_3 from Equation 7.

$$\frac{A_1}{A_2} = \frac{M_1\left[1 - \frac{\pi}{3}(I_G t_{G1} + N_q)U_G^3 t_{G1}^3\right](I_G t_{G1} + N_q)}{M_2\left[1 - \frac{\pi}{3}(I_G t_{G2} + N_q)U_G^3 t_{G2}^3\right](I_G t_{G2} + N_q)} \quad (8)$$

Simultaneous solutions of any two of the three equations for A_1/A_2, A_1/A_3, and A_2/A_3 will yield the values for N_q and I_G, which can then be used in Equation 7 as constants for determining $(I_N t_N)$.

Once the values for the nucleation rate at different temperatures are known, the crystal growth rate U_T at any temperature T can be determined easily from only two DTA runs obtained after heat treating an as-quenched glass at T for times $t_{\mathrm{T}1}$ and $t_{\mathrm{T}2}$. The following equation which is obtained after rearranging Equation 8 can be used for calculating U_T.

$$U_\mathrm{T} = \left[\frac{3\bigl(A_1 M_2(I_\mathrm{T} t_{\mathrm{T}_2} + N_\mathrm{q}) - A_2 M_1(I_\mathrm{T} t_{\mathrm{T}_1} + N_\mathrm{q})\bigr)}{\pi\bigl(A_1 M_2(I_\mathrm{T} t_{\mathrm{T}_2} + N_\mathrm{q})^2 t_{\mathrm{T}2}^3 - A_2 M_1(I_\mathrm{T} t_{\mathrm{T}_1} + N_\mathrm{q})^2 t_{T1}^3}\right]^{1/3} \tag{9}$$

where, I_T is the nucleation rate at T, which has been determined previously. Note that all the equations presented above could be simplified further if the two samples used for the two DTA runs have the same mass ($M_1 = M_2$).

3. Experimental procedure

The NC_2S_3 glass used in this investigation was prepared by melting a homogeneous mixture of a reagent grade sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$) and silica (SiO_2) in a platinum crucible at 1400°C for 3 h, stirring the melt three times during melting to ensure chemical homogeneity, and quenching the melt between two steel plates. The weight of the powdered mixture (batch) was adjusted to yield 100 g of glass. The glass was ground and screened to a particle size between 500 and 600 μm, and immediately stored in a vacuum desiccator until used. X-ray diffraction analysis (XRD) of the as-quenched glass did not show the presence of any crystalline material. The water content of the glass was not measured.

The DTA measurements were performed in a Perkin-Elmer DT-7 instrument in flowing (30 $\mathrm{cm^3/min}$) nitrogen gas using typically 50 to 60 mg of glass particles in platinum crucibles and high purity (99.99%) alumina powder as a reference material. A temperature of 670°C was used as the crystal growth temperature (T_G) for all the DTA measurements conducted for measuring I and N_q for the NC_2S_3 glass. The crystal growth rate (U_G) at 670°C, $\sim 7.57 \times 10^{-9}$ $\mathrm{ms^{-1}}$, as measured by Gonzalez-Oliver and James [1] using conventional method was used as a known (constant) parameter in all of our calculations.

Before proceeding further for measuring the rates for nucleation (I) and crystal growth (U) by DTA, it is important to determine first whether the I and U curves overlap at the temperature chosen for crystal growth (T_G). As discussed earlier, Equation 1 in its simple form can be used if no overlap between I and U is found at T_G, but Equation 7 should be used, instead, if I and U overlap at T_G.

To determine whether the I and U curves for the NC_2S_3 glass overlap at 670°C, the concentration of quenched-in nuclei, N_q, in the glass was determined using Equation 1 and the following experimental steps;

(1) heat the glass in the DTA apparatus to 670°C at 20°C/min,
(2) hold the glass at 670°C for 10, 15, or 20 min,
(3) cool to 400°C at 20°C/min and stabilize the sample at 400°C for 5 min,
(4) perform a DTA scan at 10°C/min until crystallization is complete (as determined by the presence of a DTA exotherm).

The values of N_q determined using the area of any two of the three DTA peaks obtained above (after crystal growth heat treatment at 670°C for 10, 15, or 20 min) are given in column 4 of Table I. Clearly, the N_q values in Table I, instead of being constant, depend on the choice of the heat treatment time at 670°C. These results indicate that the I and U curves overlap for the NC_2S_3 glass at 670°C and, therefore, Equation 7, not Equation 1, should be used for this glass to determine I or U as a function of temperature. The DTA patterns for the NC_2S_3 glass, measured at a heating rate of 10°C/min after heat treatment at 670°C for 10, 15, or 20 min, are shown in Fig. 2.

For comparison, the N_q values for a LS_2 glass were also determined in a similar way as described above using a crystal growth temperature of 600°C and are reported in column 3 of Table I. A crystal growth rate of 2.5×10^{-8} $\mathrm{m\,s^{-1}}$ measured by Gonzalez-Oliver *et al.* [9] using conventional method for the LS_2 glass at 600°C was used for the calculations. The LS_2 glass was prepared in the same way as described for the NC_2S_3 glass. Unlike the N_q values for the NC_2S_3 glass (column 4, Table I), the values of N_q for the LS_2 glass (column 3, Table I) as determined by DTA and using Equation 1 are independent of the time for heat treatment at 600°C, which suggests that the I and U curves for the LS_2 glass have no or negligible overlap at 600°C.

Taking the ratio of the DTA peak areas obtained above for the NC_2S_3 glass (Fig. 2), three equations of the type given in Equation 8 were then developed for A_{10}/A_{15}, A_{10}/A_{20}, and A_{15}/A_{20}, where A_{10}, A_{15}, and A_{20} are the area of the DTA peaks obtained after heat treatment (at 670°C) for 10, 15, and 20 min, respectively. A simultaneous solution of any two of these three equations yield the values for N_q and I_{670} (nucleation rate at the crystal growth temperature 670°C). The results are given in colums 2 and 4, respectively, of Table II. As done before, the crystal growth rate, U_G, at 670°C was assumed to be 7.6×10^{-8} $\mathrm{m\,s^{-1}}$. As shown in Table II, the value of N_q or I_{670} is nearly constant irrespective of which two of the three equations were used for the calculations. The average of N_q and I_{670} shown in Table II are 2.7×10^{14} $\mathrm{m^{-3}}$ and 7.3×10^{10} $\mathrm{m^{-3}s^{-1}}$, respectively, which are used as known constants in Equation 7 for calculating I or U at different temperatures.

To investigate the reproducibility of the results and validity of the DTA approach, values of N_q and I_G were also determined from DTA runs after heat treatment at another temperature (T_G), 700°C, for 10, 15, or 20 min. The results are shown in columns 3 and 5, respectively, of Table II. The crystal growth rate (U_G) at 700°C, 2.50×10^{-8} $\mathrm{m\,s^{-1}}$, was, once again, taken from Ref. 1. As shown in Table II, the values of N_q determined from DTA using a crystal growth temperature

TABLE II Concentration of quenched-in nuclei (N_q) and nucleation rate (I_G) for the NC_2S_3 glass measured by DTA using 670° or 700°C as the crystal growth temperature (T_G)

Ratio of DTA peak areas whose corresponding equations (like Equation 8) were used for calculations	N_q (m^{-3})		Nucleation rate (I_G) ($m^{-3}s^{-1}$)	
	$T_G = 670°C$	$T_G = 700°C$	$T_G = 670°C$ (I_{670})	$T_G = 700°C$ (I_{700})
(A_{10}/A_{15}) and (A_{15}/A_{20})	2.8×10^{14}	2.9×10^{14}	7.5×10^{10}	2.6×10^{10}
(A_{10}/A_{20}) and (A_{15}/A_{20})	2.6×10^{14}	2.9×10^{14}	7.4×10^{10}	2.8×10^{10}
(A_{10}/A_{20}) and (A_{10}/A_{15})	2.7×10^{14}	2.7×10^{14}	7.0×10^{10}	2.9×10^{10}

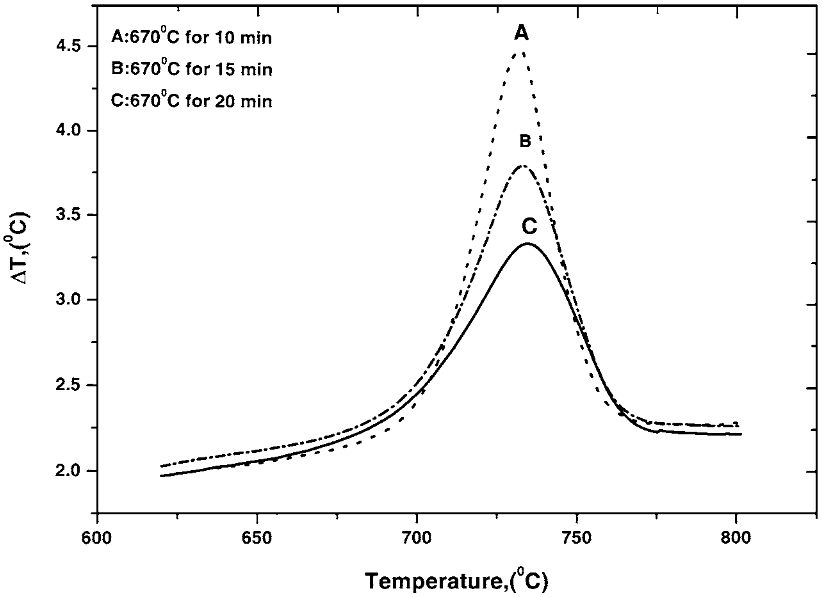

Figure 2 DTA curves for $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass heated at 10°C/min after heat treating at 670°C for (A) 10 min, (B) 15 min, or (C) 20 min. Sample weight:50 mg.

of either 670°C (column 2) or 700°C (column 3) are in excellent agreement. This agreement demonstrates the usefulness and validity of the DTA approach and the correctness of the modified Equation 8 to determine the concentration of quenched-in nuclei (N_q) in glasses even when their I and U curves overlap considerably. The value of I at 700°C is nearly constant when calculated using any two of the three equations for the ratio of the DTA peak areas, compare the different values in column 5 of Table II. The average value of I_{700} is about 2.5 times smaller than the average value of I_{670} (compare columns 4 and 5), which is consistent with the fact that the value of I in the region of overlap between I and U decreases with increasing temperature.

3.1. Heat treatment cycles for measuring the nucleation rate (I)

The following heat treatment cycles were used to measure the nucleation rate, I, as a function of temperature.

(1) Heat the glass particles in the DTA furnace to 590°C (T_N) at 20°C/min,

(2) hold at 590°C for 1 hr (t_N)—nucleation heat treatment,

(3) heat from 590°C to 670°C (T_G) at 20°C/min,

(4) hold at 670°C for 10 min (t_{G1})—crystal growth heat treatment,

(5) cool to 400°C at 20°C/min and stabilize the sample at 400°C for 5 min,

(6) heat at 10°C/min until crystallization is complete as indicated by a DTA exothermic peak of area A_1,

(7) using a new sample, repeat all of the steps above except the heat treatment time at 670°C is 20 min (t_{G2})—DTA peak area A_2.

From the experimental values of A_1 and A_2, the number of nuclei (It_N) developed for nucleation at 590°C for 1 h can be determined using Equation 7, since the values for N_q, I_G (at 670°C), and U_G (at 670°C) are known.

(8) Repeat all of the above steps except the heat treatment time for nucleation in step 2, t_N is 4, 6, or 10 h and obtain (It_N) as a function of t_N. The slope of the plot (It_N) vs t_N yields the nucleation rate, I at 590°C.

(9) Repeat all of the experimental steps for the nucleation temperatures, $T_N = 600$, 610, 620, 630, 640, and 655°C to determine I as a function of temperature.

3.2. Heat treatment cycle for measuring the crystal growth rate, (U)

Once the values for I at different temperature are determined and since N_q is already known, the crystal growth rate at any temperature can be determined from just two DTA runs at each temperature (no nucleation heat treatment is necessary). The following heating cycles were used to determine U as a function of temperature in the present investigation.

(1) Heat the glass particles in DTA to 620°C at 20°C/min,

(2) hold at 620°C for 10 min (t_{T1})—crystal growth heat treatment,

(3) cool to 400°C at 20°C/min and stabilized the sample at 400°C for 5 min,

(4) heat at 10°C/min until crystallization is complete (DTA peak area—A_1),

(5) using a new sample, repeat all of the above steps except the heat treatment time at 620°C in step 2 is 20 min (t_{T2}) (DTA peak area—A_2).

From the experimental values of A_1 and A_2, the crystal growth rate at 620°C can be determined using Equation 9 and the already determined values of I (at 620°C) and N_q.

(6) Repeat all of the above experimental steps for different crystal growth temperatures (630, 640, and 655°C) to determine U as a function of temperature.

4. Results and discussion

4.1. Nucleation rate (I)

The DTA peak areas measured using the procedures outlined in Section 3 (experimental procedure, 1. heat treatment cycle for measuring the nucleation rate) were used to calculate (Equation 7), the total number of nuclei (It_N) formed in the NC_2S_3 glass during nucleation at 590, 600, 610, 620, 630, 640 and 655°C for various nucleation times (t_N). Typical (It_N) vs. t_N plots for three representative nucleation temperatures, 590, 610, and 655°C are shown in Fig. 3. The lines are the linear fits of the experimental data points, whose slope yields the nucleation rate, I, at the respective temperatures. As shown in Fig. 3, the nucleation rate first increased as the temperature increased from 590 to 600°C and then decreased as the temperature increased to 655°C. The values of I at different temperatures determined by the present DTA method for this NC_2S_3 glass are shown at the inset, which has the usual bell-shaped form with a temperature for a maximum nucleation rate at 606 ± 3°C.

The straight lines through the data points at 590 or 600°C in Fig. 3 intercept the time axis at about 30 min, which may be considered as the induction time, t_{ind}, for nucleation for the NC_2S_3 glass over this temperature range. No induction time is involved at 655°C, which is expected since t_{ind} rapidly decreases with increasing temperature. The 30 min induction time determined by the present DTA method at 590, 600, or 655°C for this NC_2S_3 glass is consistent with the t_{ind}-values (<1 h) measured by conventional method [1–4, 8, 10]. However, considering the scatter at each temperature in the data points in Fig. 3 and the small value of t_{ind} at these temperatures, the accuracy for the induction time determined by DTA in the present investigation for the NC_2S_3 glass cannot be fully assured.

The values of I determined by DTA at different temperatures for the NC_2S_3 glass have been compared in Fig. 4 with those determined by others [1–4] using the conventional method. The unit of I, namely, log (I, mm^{-3} min^{-1}), in Fig. 4 was chosen for making a direct comparison, since most references have used this unit to report the value of I for the NC_2S_3 glass. The dashed line in Fig. 4 represents the average of all the I-values determined by different investigators using the conventional method. The solid line is the smooth curve for the I-values from the present DTA work. As shown in Fig. 4, the values of I determined by the DTA method is generally in very good agreement with the I-values determined by the conventional method. It is noted, also, that the I-values determined by the DTA method (solid lines in Fig. 4) are little lower (<8% in log I) than the I-values determined by the conventional method (dashed line in Fig. 4). However, considering

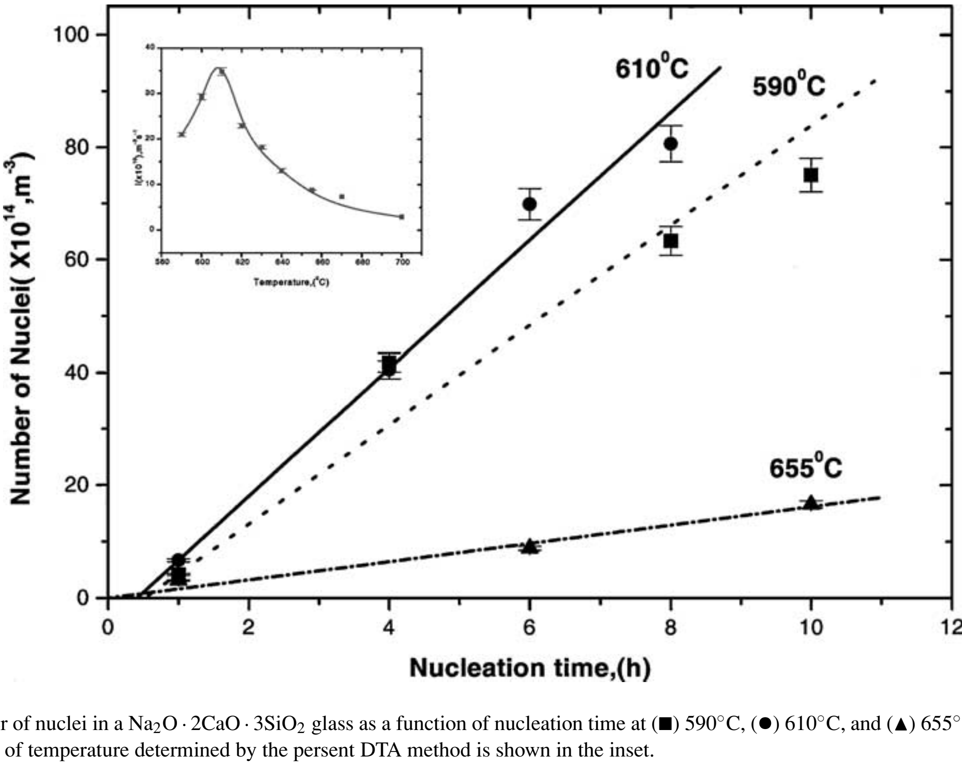

Figure 3 Number of nuclei in a $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass as a function of nucleation time at (■) 590°C, (●) 610°C, and (▲) 655°C. The nucleation rate as a function of temperature determined by the persent DTA method is shown in the inset.

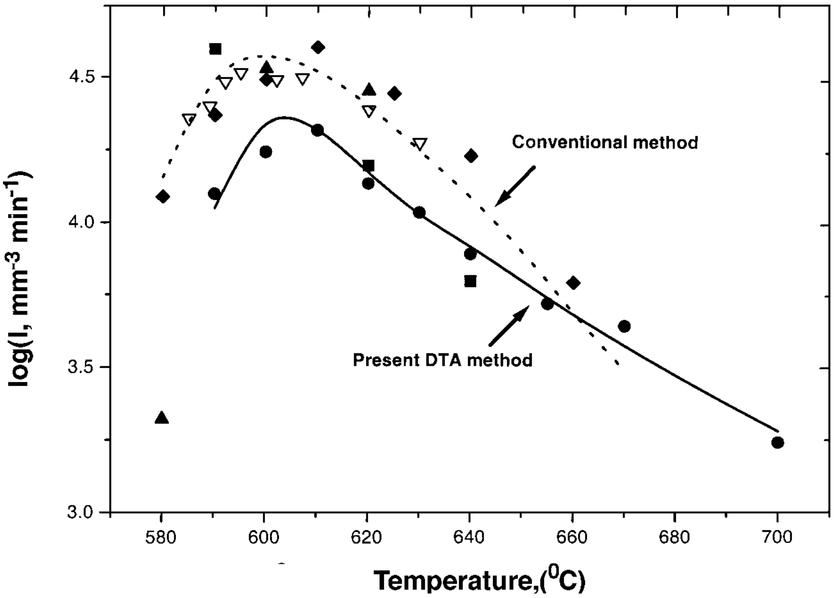

Figure 4 Comparison of the steady state nucleation rate (I) determined as a function of temperature by the present DTA method with those determined by the conventional method for the $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass:(-●-) present DTA method, (■) Ref. 1, (◆) Ref. 2, (▲) Ref. 3, and (▽) Ref. 4. Solid line is the average of the results from the DTA method and the dashed line is the average of all the results from conventional methods.

the magnitude of error involved in the conventional measurements, see solid squares [1] for example, this difference in I-values from the DTA and conventional measurements is not significant.

In the case of conventional measurements, the formation of additional nuclei during the crystal growth heat treatment cannot be avoided if the crystal growth temperature is in the temperature region where I and U overlap. These additional nuclei, which simultaneously grow to crystals, are inadvertently included in the count for the total number of nuclei (per unit volume), which may introduce error in the measured values of I if the time at the crystal growth heat treatment temperature is not maintained a constant for all the experiments. The present DTA method takes account for the effect of nucleation at the crystal growth temperature and eliminates it from the effect of total nucleation, see Equations 7 and 8. Thus, the values of I determined by DTA at different temperatures for this NC_2S_3 glass are believed to be reasonably accurate.

4.2. Crystal growth rate (U)

The crystal growth rate, U, determined at 620,630,640 and 655°C for the NC_2S_3 glass by DTA is shown in Fig. 5, along with the U-values reported in the literature [1–4] in this temperature range. U in the present work was determined using Equation 9 and the peak areas (A_1 and A_2) for two DTA runs that were obtained after crystal growth heat treatments at each temperature for

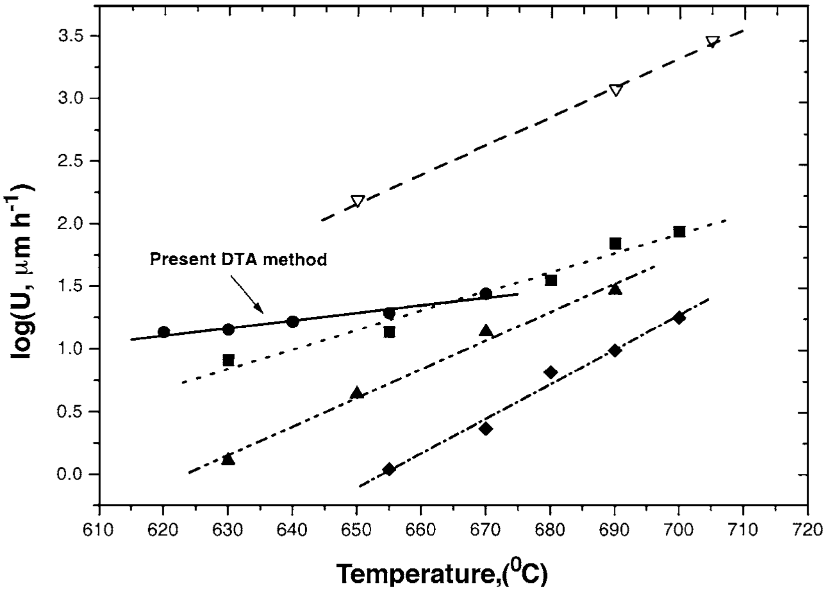

Figure 5 Comparison of crystal growth rate(U) as a function of temperature determined by the present DTA method with those determined by the conventional method for the $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass: (-●-) present DTA method, (■) Ref. 1, (◆) Ref. 2, (▲) Ref. 3, and (▽) Ref. 4.

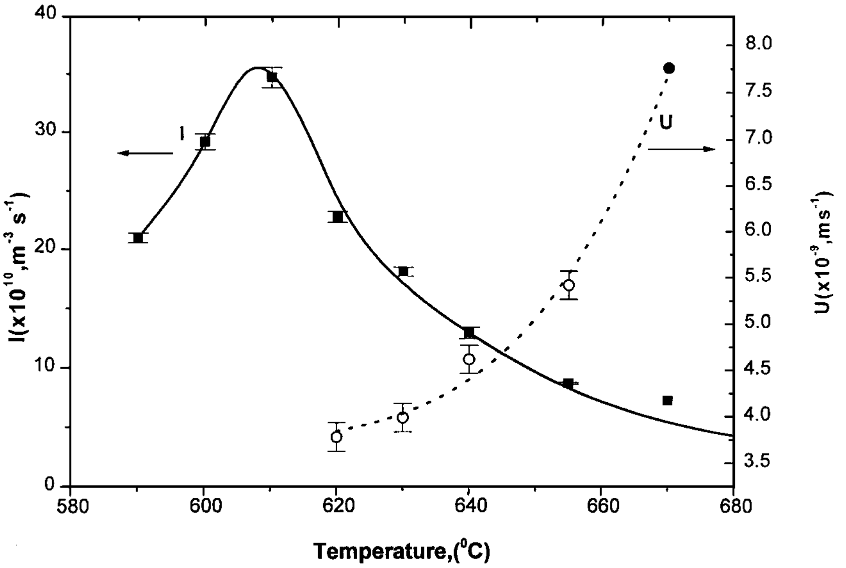

Figure 6 Nucleation (I) and crystal growth (U) rates as a function of temperature determined by the present DTA method for $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass, showing the overlap between I and U. The solid circle in the U data is from Ref. 1.

10 (t_{T1}) or 20 (t_{T2}) min. A previously determined value of N_q, namely, 2.7×10^8 m^{-3} (average of all N_q values in Table II) was used in Equation 9. The nucleation rate (I_T) at 620, 630, 640, and 655°C was taken from the I values already determined as a function of temperature, see above and the inset in Fig. 3. As mentioned earlier, the crystal growth rate at 670°C measured by Gonzalez-Oliver and James [1] was used as a known parameter to determine N_q and I (as a function of temperature) in the present investigation, so this particular value of the crystal growth rate (U at 670°C) belongs to both set of data points (Fig. 5); the data points for the present DTA method and those measured by Gonzalez-Oliver and James [1].

As shown in Fig. 5, the crystal growth rate for the NC_2S_3 glass measured by different investigators using the conventional method varies considerably, and the values of U determined in the present work fall within the range of values reported [1, 4]. The rate of increase in U with increasing temperature (slope of the straight lines), however, is smaller in the present investigation than for any of the results for conventional measurements. The reason for this difference is not clearly understood at this time.

In order to estimate the extent of overlap between the I and U curves, the I and U values determined by the present DTA method for the NC_2S_3 glass are shown in Fig. 6 as a function of temperature. A considerable overlap of the I and U curves is obvious for this glass. An extended U to lower temperatures indicates that crystal growth starts almost from the temperature where the nucleation rate (606 ± 3°C) is a maximum. Measurements by the conventional method [1] also show that the crystal growth rate for this NC_2S_3 glass starts at about 610°C where the nucleation rate for this glass is observed [2, 3] to be a maximum. The present DTA method, therefore, appears to be very effective and useful in determining the extent of overlap between the I and U curves of a glass.

5. Conclusion

A generalized method based on differential thermal analysis (DTA) for quantitatively determining the rates for nucleation (I) and crystal growth (U) as a function of temperature, and the concentration of quenched-in nuclei (N_q) in glasses has been developed. The method is applicable to all glasses, whether or not their I and U curves overlap on the temperature scale. This generalized DTA method is about 10 times faster and requires much less sample (about 1/15th) than the conventional method. Also, the special sample preparation such as cutting, grinding, polishing, and etching which is required in the conventional method, is not necessary in this DTA method, with the exception of grinding the sample to particles of suitable size. For a $Na_2O \cdot 2CaO \cdot 3SiO_2$ glass, whose I and U curves are known to overlap significantly, the nucleation and crystal growth rates, determined as a function of temperature by the present DTA method, are in excellent agreement with those determined by conventional methods. Thus, this DTA method provides a rapid and alternative means for determining the nucleation and crystal growth rates in glasses, even when these rate curves overlap on the temperature scale.

The present DTA method also provides a way to quickly determine whether the I and U curves of a glass overlap or not. The experimental approach for determining I and U is further simplified and less time consuming when the I and U curves do not overlap, compared to when they overlap to some degree. For an unknown glass, therefore, it is recommended that any overlap in the I and U curves be determined first, particularly, at the temperature chosen for crystal growth. Then whatever experimental approach is necessary for determining I or U should be followed.

References

1. C. J. R. GONZALEZ-OLIVER and P. F. JAMES, *J. Non-Cryst. Solids*. **38&39** (1980) 699.

2. O. V. POTPOV, V. M. FOKIN, V. N. FILIPOVICH and A. M. KALININA, *Glass Physics and Chemistry* **24**(4) (1998) 337.
3. J. DEUBENER and R. BRUKNER, *J. Non-Cryst. Solids* **163** (1993) 1.
4. K. L. NARAYAN and K. F. KELTON, *ibid.* **220** (1997) 222.
5. V. M. FOKIN, O. V. POTPOV, C. R. CHINAGLIA and E. D. ZANOTTO, *ibid.* **258** (1999) 180.
6. Z. STRAND and R. W. DOUGLAS, *Phys. Chem. Glass* **14**(2) (1973) 33.
7. O. V. POTPOV, V. M. FOKIN and V. N. FILIPOVICH, *J. Non-Cryst. Solids* **247** (1999) 74.
8. O. V. POTPOV, V. M. FOKIN, V. L. UGOLKOV, L. Y. SUSLOVA and V. N. FILIPOVICH, *Glass Physics and Chemistry* **26**(1) (2000) 27.
9. C. J. R. GONZALEZ-OLIVER, P. S. JOHNSON and P. F. JAMES, *J. Mater. Sci.* **14** (1979) 1159.
10. G. L. SMITH and M. C. WEINBERG, *J. Phys. Chem. Glasses.* **32**(2) (1991) 37.
11. C. S. RAY, X. FANG and D. E. DAY, *J. Amer. Ceram. Soc.* **83** (2000) 865.
12. E. D. ZANOTTO and A. GALHARDI, *J. Non-Cryst. Solids* **104** (1988) 73.
13. E. D. ZANOTTO, *ibid.* **129** (1991) 183.

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