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A study on the variations in the density of nucleated particles with the maximum crystallization rate and with the corresponding temperature, by using differential scanning calorimetry

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Abstract

An analysis is carried out on two procedures which have been proposed for the determination of the temperature dependence of homogeneous crystal nucleation rates in glassy solids by using differential scanning calorimetry (DSC) measurements. The first procedure is based upon the hypothesis that the density of nucleated particles will increase monotonically as the reciprocal of the temperature corresponding to the maximum crystallization rate increases. The second procedure is based on the observation that the maximum crystallization rate increases as the corresponding temperature grows. The validity of both procedures is assessed for glassy solids by considering two specific crystal growth models.

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1. Introduction

Knowledge of amorphous materials is one of the most active fields of research in the physics of condensed matter today [1]. The great interest in these materials is largely due to their ever increasing applications in modern technology. Their possibilities in the immediate future are huge based on characteristic properties such as electronic-excitation phenomena, chemical reactivity and inertia, and superconductivity. Therefore, the advances that have been made in physics and chemistry of the quoted materials during the last 40 years have been very appreciated within the research community. Among the different techniques used to the study of the glassy solids, the differential thermal analysis (DTA) and the differential scanning calorimetry (DSC) have promoted an intense theoretical and practical interest. The quoted techniques have been used extensively for the study of the kinetics of phase transformation processes and chemical reactions [2]. In the field of glass science, these experimental procedures have been employed for the determination of glass-forming ability of compositions, critical cooling rates [3–5] and for the investigation of the crystallization kinetics of glasses [6–8]. Also, DSC studies have been performed for the purpose of measuring homogeneous crystal nucleation rates in glasses [9,10]. The study of the glass-crystal transformation has often been limited by the elaborate nature of the experimental procedures that are employed. The increasing use of the quoted thermoanalytical techniques offers the promise of obtaining useful data with simple methods.

The utilization of thermoanalytical techniques depends in turn on the development of sound methods for analyzing the experimental data. With this objective, a large number of mathematical treatments have been proposed for analyzing DTA and DSC data. These treatments have been fraught with controversy and have led to the formulation of many (slightly) different equations for the analysis of such data. Several of these formulations have been reviewed and critically analyzed by Yinnon and Uhlmann [11]. In the last decade, it has been indicated that the previous treatments have assumed a reaction rate constant, $K(T)$, of Arrhenius type, and an analysis was given to delineate the conditions

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under which this assumption could be used for the interpretation of certain simple crystallization processes [12].

In the present work are examined some of the standard assumptions which have been used in the analysis of DSC experiments performed for the purpose of measuring the homogeneous crystal nucleation rates in the glasses. The procedure, which can be used for the determination of nucleation rates by means of DSC experiments, described in the literature [9], it is essentially the following. A glass is heated isothermally (in the DSC apparatus) for a given time period at a low temperature to promote crystal nucleation. Next, the glass is subjected to a non-isothermal heating at a constant rate to crystallize the sample, and the non-isothermal thermogram is recorded. The procedure is subsequently repeated using identical nucleation temperature, but different time periods. This thermal treatment will produce a family of thermograms exhibiting different peak temperatures of maximum crystallization, T_{p}, and different maximum crystallization rates, $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$. These variations in the quantities T_{p} and $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ suggest an analysis of the relationship between the quoted quantities and the number of nuclei/length, N. In this work, the increase in N with T_{p}^{-1} and $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ is justified for two standard crystal growth models, normal and screw dislocation growth, not assuming a crystal growth rate of Arrhenius type, but under more general conditions. Finally, as a verification example, from data taken of literature [9], two good linear relationships have been found, both between $\ln N$ and T_{p}^{-1} and between $\ln(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ and $\ln N$, for the lithium disilicate glass nucleation.

2. Nucleation, crystal growth and volume fraction transformed

The theoretical basis for interpreting DTA or DSC results is provided by the formal theory of transformation kinetics [13–20]. This theory is largely independent of the particular models used in detailed descriptions of the transformation mechanisms, and supposes that the crystal growth rate, in general, is anisotropic. This rate in any direction can be then represented in terms of the principal growth velocities, u_i ($i = 1, 2$ and 3) in three mutually perpendicular directions [21]. In these conditions the one dimensional growth in an elemental time, $\mathrm{d}t'$, can be expressed as $u_i(t')\,\mathrm{d}t'$, and this growth for a finite time is $\int_\tau^t u_i(t')\,\mathrm{d}t'$.The volume of a region originating at time $t = \tau$ (τ being the nucleation period) is then

$$v_\tau = g\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t' \tag{1}$$

where the expression $\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'$condenses the product of the integrals corresponding to the values of the above quoted subscript i and g is a geometric factor, which depends on the dimensionality and shape of the crystal growth, and therefore its dimension equation can be expressed as

$$[g] = [L]^{3-i} \quad ([L]\,\text{is the length})$$

Defining and extended volume of transformed material and assuming spatially random nucleation [21,22], the elemental extended volume fraction in terms of nucleation frequency per unit volume, $I_{\mathrm{v}}(\tau)$, is expressed as

$$\mathrm{d}x_{\mathrm{e}} = v_\tau I_{\mathrm{v}}(\tau)\,\mathrm{d}\tau = gI_{\mathrm{v}}(\tau)\left(\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'\right)\mathrm{d}\tau \tag{2}$$

bearing in mind the relation $\mathrm{d}x = (1-x)\,\mathrm{d}x_{\mathrm{e}}$ and integrating the resulting expression, one obtains

$$-\ln(1-x) = g\int_0^t I_{\mathrm{v}}(\tau)\left[\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'\right]\mathrm{d}\tau \tag{3}$$

where x is the true volume fraction transformed.

When the crystal growth rate is isotropic, $u_i = u$, an assumption which is in agreement with the experimental evidence, since in many transformations the reaction product grows approximately as spherical nodules [23], Eq. (3) can be written as

$$-\ln(1-x) = g\int_0^t I_{\mathrm{v}}(\tau)\left[\int_\tau^t u(t')\,\mathrm{d}t'\right]^m \mathrm{d}\tau \tag{4}$$

where m is an exponent, which depends on the dimensionality of the crystal growth.

With the aim of interpreting the thermal experiments used for crystal nucleation rate determinations, two assumptions must are made, which appear to be in accord with the experimental conditions, which are used in the above-mentioned experiments. First, it is considered that all nucleation is completed prior to crystal growth. If the temperature region in which nucleation is non-negligible is narrow (which is usually the case for homogeneous crystal nucleation) and/or sufficiently large non-isothermal heating rates are used, then one can ensure that there is virtually no nucleation occurring during the non-isothermal heating. Also, since in many glass systems the crystal growth rates are extremely small at nucleation temperatures, one can often assume that the volume fraction crystallized during the isothermal nucleation step is virtually zero (see Fig. 1) [19]. Thus, the condition of “site saturation” [24,25] is physically realistic.

Second, it is assumed that only one transformation mechanism occurs, namely, homogeneous crystal nucleation. It is known that many glasses which exhibit homogeneous crystal nucleation also surface crystallize. However, it can be indicated, according to the literature [9], that by proper control of particle size one can suppress surface crystallization, and thus one can study bulk nucleation.

When the first assumption is considered, Eq. (4) can be written as

$$-\ln(1-x) = gN^m\left[\int_0^t u(t')\,\mathrm{d}t'\right]^m \tag{5}$$

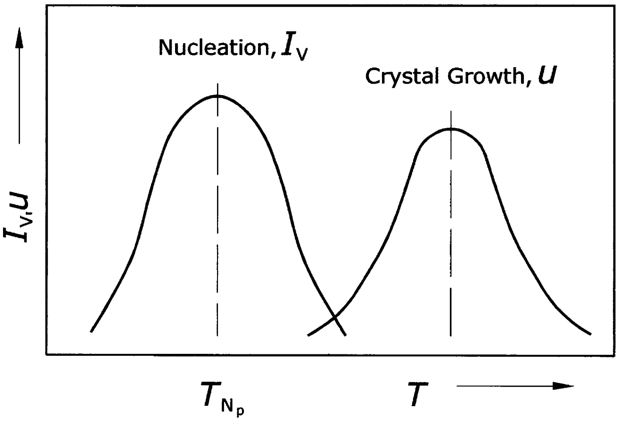

Fig. 1. Schematic representation of the temperature-dependent rates of nucleation and crystal growth, when the quoted processes occur in separate stages.

N^m being the number of nuclei/(length)^m and where the integral has been evaluated between 0 and t, since there is no nucleation period, $\tau = 0$.

Bearing in mind that a linear heating rate, β, is usually employed in non-isothermal experiments, then $T = T_0 + \beta t$, where T_0 is the initial temperature of the thermal treatment and therefore $\mathrm{d}t = \mathrm{d}T/\beta$, and Eq. (5) can be rewritten in exponential form as

$$\begin{aligned} x &= 1 - \exp\left\{-g\left[r\int_{T_0}^{T} u(T')\,\mathrm{d}T'\right]^m\right\} \\ &= 1 - \exp\left[-g(rI)^m\right] \end{aligned} \tag{6}$$

with $r = N/\beta$, N being the number of nuclei/length. It should be noted that Eq. (6) is a general expression of the volume fraction crystallized for all possible values of the m exponent, which, as is well known, depends on the dimensionality of the crystal growth.

The crystallization rate is obtained by deriving the volume fraction crystallized with respect to time, and substituting in the resulting expression the exponential function by its value given in Eq. (6), results in

$$\frac{\mathrm{d}x}{\mathrm{d}t} = gm\beta r^m (1-x) I^{m-1} u(T) \tag{7}$$

The maximum crystallization rate is found by making $\mathrm{d}^2x/\mathrm{d}t^2 = 0$, yielding

$$(rI_p)^m = \frac{1}{mg}\left(m - 1 + \frac{\dot{u}_p}{\beta u_p^2} I_p\right), \left(\dot{u} = \frac{\mathrm{d}u}{\mathrm{d}t}\right) \tag{8}$$

where the subscript p denotes the quantity values corresponding to the maximum crystallization rate.

By assuming an Arrhenian temperature dependence for $u(T)$, Eq. (8) becomes

$$(rI_p)^m = \frac{1}{mg}\left(m - 1 + \frac{E}{RT_p^2}\frac{I_p}{u_p}\right) \tag{9}$$

where $I_p = \int_{T_0}^{T_p} u_0 \exp(-E/RT)\,\mathrm{d}T$, according to Eq. (6). By using the substitution $y = E/RT$ the integral I_p can be evaluated as the sum of the alternating series [26]

$$S(y_p, y_0) = \left[-\mathrm{e}^{-y} y^{-2} \sum_{k=0}^{\infty} \frac{(-1)^k (k+1)!}{y^k}\right]_{y_0}^{y_p} \tag{10}$$

where it is possible to use only the first term, without making any appreciable error, obtaining

$$I_p \approx u_0 E R^{-1} \mathrm{e}^{-y_p} y_p^{-2} = u_0 R T_p^2 E^{-1} \exp\left(\frac{-E}{RT_p}\right) \tag{11}$$

if it is assumed that $T_0 \ll T_p$, so that y_0 can be taken as infinity. This assumption is justifiable for any heating treatment that begins at a temperature where the crystal growth is negligible, i.e., below T_g (glass transition temperature) for most glass-forming systems [11].

Substituting Eq. (11) into Eq. (9), the logarithmic form of resulting expression may be written as

$$\ln N = \ln\beta - \ln T_p^2 + \frac{E}{RT_p} + \ln[E(u_0 R g^{1/m})^{-1}] \tag{12}$$

Moreover, it should be noted that the change of $\ln T_p^2$ with β is negligibly small compared with the change of $\ln\beta$, and therefore it is possible to obtain

$$\ln N = \ln\beta + \frac{E}{RT_p} + \text{constant} \tag{13}$$

an identical expression to that given in the literature [10]. Thus, for constant heating rate, the logarithm of the number of nuclei should be inversely proportional to the temperature corresponding to the maximum crystallization rate. However, there is one potential difficulty with the use of this development, since this method makes the assumption that $u(T)$ is of Arrhenius type, which may not be justified under all conditions. Bearing in mind this fact we analyze the relationships: $N = f_1(T_p^{-1})$ and $N = f_2[(\mathrm{d}x/\mathrm{d}t)|_p)]$ under more general conditions.

2.1. Analyzing the relationship between N and T_p^{-1}

In this section it is analyzed whether N must increase with T_p^{-1} in all cases. If the density of nucleated particles always increases with increasing T_p^{-1}, then $\mathrm{d}N/\mathrm{d}T_p^{-1}$ should always be greater than zero. Bearing in mind that $r = N/\beta$, results in

$$\frac{\mathrm{d}N}{\mathrm{d}T_p^{-1}} = \beta\frac{\mathrm{d}r}{\mathrm{d}T_p}\frac{\mathrm{d}T_p}{\mathrm{d}T_p^{-1}} = -\beta T_p^2 \frac{\mathrm{d}r}{\mathrm{d}T_p}$$

which imply that $\mathrm{d}r/\mathrm{d}T_p < 0$ in general. Therefore, this latter hypothesis must be tested. First, with the aim of considering the bulk crystallization Eq. (8) becomes

$$(rI_p)^3 = \frac{1}{4\pi}\left(2 + \frac{\dot{u}_p}{\beta u_p^2} I_p\right) \tag{14}$$

by using $m = 3$ and the geometric factor $g = 4\pi/3$. It should be noted that by an inspection of Eq. (14) it is clear that the specific temperature dependence of the crystal growth rate will affect the conclusion. However, the choice of a specific temperature dependence for u will be deferred until later. Accordingly, taking the derivative of Eq. (14) with respect to T_p, one obtains

$$3r^2 I_p^3 \frac{\mathrm{d}r}{\mathrm{d}T_p} = \frac{1}{4\pi\beta}\left[\left(1-\frac{\dot{u}_p}{u_p^2}\frac{I_p}{\beta}\right)\frac{\dot{u}_p}{u_p} + \left(\ddot{u}_p - \frac{\dot{u}_p^2}{u_p}\right)\frac{I_p}{\beta u_p^2}\right] - 3r^3 I_p^2 u_p \tag{15}$$

Given that $I_p > 0, 3r^2 I_p^3 > 0$ and, therefore, $\mathrm{d}r/\mathrm{d}T_p$ must be of equal sign that the right side of Eq. (15).The above-mentioned right side one may write as the sum of two terms:

$$A_1 = \frac{1}{4\pi\beta}\left(1-\frac{\dot{u}_p}{u_p^2}\frac{I_p}{\beta}\right)\frac{\dot{u}_p}{u_p} - 3r^3 I_p^2 u_p \tag{16}$$

and

$$A_2 = \frac{1}{4\pi\beta}\left(\ddot{u}_p - \frac{\dot{u}_p^2}{u_p}\right)\frac{I_p}{\beta u_p^2} \tag{17}$$

It should be noted that the sign of both terms must be determined, and thus, the sign of the term A_1 can be analyzed by substituting in Eq. (16) the values of terms $(\dot{u}_p/u_p^2)(I_p/\beta)$ and $\dot{u}_p/u_p$, given in Eq. (14), yielding

$$A_1 = -\frac{u_p I_p^{-1}}{2\pi}(8\pi^2 v_p^2 - 4\pi v_p + 3) \tag{18}$$

where $v_p = (rI_p)^3$. Given that both I_p and u_p are positive quantities, and the quadratic form $8\pi^2 v_p^2 - 4\pi v_p + 3$ is positive for all real values of v_p, the term A_1 is, in general, negative.

The algebraic sign of A_2, however, depends on the specific crystal growth model which is selected. Nevertheless, a fairly general condition may be extracted for which $A_2 < 0$.The term A_2 can be written as follows:

$$A_2 = \frac{1}{4\pi\beta}\frac{I_p}{u_p}\frac{\ddot{u}_p u_p - \dot{u}_p^2}{\beta u_p^2} = \frac{1}{4\pi\beta}\frac{I_p}{u_p}\frac{\mathrm{d}}{\mathrm{d}T_p}\left(\frac{\dot{u}_p}{u_p}\right) \tag{19}$$

All three of the standard crystal growth models (normal growth, screw dislocation growth, and surface nucleated growth) are of the form [11]

$$u(T) = u_0 \eta^{-1} H \tag{20}$$

where u_0 is a constant, η is the viscosity, and H is some function of temperature. By substituting Eq. (20) into Eq. (19), one obtains

$$A_2 = \frac{1}{4\pi}\frac{I_p}{u_p}\frac{\mathrm{d}}{\mathrm{d}T_p}\left[\frac{\eta_p^{-1}(\mathrm{d}H_p/\mathrm{d}T_p) - \eta_p^{-2}H_p(\mathrm{d}\eta_p/\mathrm{d}T_p)}{\eta_p^{-1}H_p}\right] = \frac{1}{4\pi}\frac{I_p}{u_p}\left(\frac{\mathrm{d}^2(\ln H_p)}{\mathrm{d}T_p^2} - \frac{\mathrm{d}^2(\ln \eta_p)}{\mathrm{d}T_p^2}\right) \tag{21}$$

If the viscosity is of Fulcher form $\eta = \exp[\alpha + \gamma/(T - T_0)]$, where α and γ are constants, then $[\mathrm{d}^2(\ln \eta_p)]/\mathrm{d}T_p^2 \le 0$, and a sufficient condition for $A_2 < 0$ is that $[\mathrm{d}^2(\ln H_p)]/\mathrm{d}T_p^2 > 0$. However, the latter condition is not generally valid, and thus one must examine specific crystal growth models. For normal growth

$$H = 1 - \exp\left[\frac{-S(T_m - T)}{T}\right] = 1 - \mathrm{e}^S \mathrm{e}^{-ST_m/T} = 1 - A\exp\left(-\frac{B}{T}\right) \tag{22}$$

where S is the entropy of fusion in units of the gas constant and T_m is the melting temperature. One may easily obtain that

$$\frac{\mathrm{d}^2(\ln H_p)}{\mathrm{d}T_p^2} = -H_p^{-1}\left[H_p^{-1}\left(\frac{\mathrm{d}H_p}{\mathrm{d}T_p}\right)^2 - \frac{\mathrm{d}^2 H_p}{\mathrm{d}T_p^2}\right] \tag{23}$$

Taking the first and second derivative of the function H_p, with respect to T_p, gives

$$\frac{\mathrm{d}H_p}{\mathrm{d}T_p} = BT_p^{-2}(H_p - 1) \tag{24}$$

and

$$\frac{\mathrm{d}^2 H_p}{\mathrm{d}T_p^2} = BT_p^{-3}(H_p - 1)(BT_p^{-1} - 2) \tag{25}$$

Substituting Eqs. (24) and (25) into Eq. (23) the following expression is obtained

$$\frac{\mathrm{d}^2(\ln H_p)}{\mathrm{d}T_p^2} = BT_p^{-3}H_p^{-2}(H_p - 1)(BT_p^{-1} - 2H_p) = -ABT_p^{-3}H_p^{-2}\left[\exp\left(-\frac{B}{T_p}\right)\right] \times \left\{\frac{B}{T_p} - 2\left[1 - A\exp\left(-\frac{B}{T_p}\right)\right]\right\} \tag{26}$$

Moreover, by defining the quantity within braces in Eq. (26) as $g(z_p) = g(B/T_p)$, then $g(z_p)$ has a minimum value at $z'_p = S + \ln 2$, and also, one finds that the above-mentioned minimum value is $g(z'_p) = S - 1 + \ln 2 = S - 0.307$. According to Eq. (26), if $S > 0.307$, $[\mathrm{d}^2(\ln H_p)]/\mathrm{d}T_p^2 < 0$, which in turn proves that the term $A_2 < 0$. Hence, one may affirm that, for a material with viscosity of Fulcher form, and normal crystal growth, the term $\mathrm{d}r/\mathrm{d}T_p$ is negative, and therefore $\mathrm{d}N/\mathrm{d}T_p^{-1}$ will be positive and the density of nucleated particles will increase with T_p^{-1}.

Nevertheless, most of the non-metallic materials with $S > 0.307$ exhibit normal crystal growth behavior, but do not exhibit homogeneous crystal nucleation behavior. As examples we quote, according to the literature [27], SiO_2 and GeO_2, which have S values of 0.9 and 1.31, respectively. On the other hand, it has been observed that the reduced homogeneous crystal nucleation temperatures, $T_r = T/T_m$, of all inorganic glasses which nucleate homogeneously are in excess of 0.5. From the definition of the quantity $z_{\mathrm{p}} = ST_{\mathrm{m}}/T_{\mathrm{p}}$, according to Eq. (26), and considering the z'_{p} value for which the function $g(z_{\mathrm{p}})$ takes the minimum value, one concludes that

$$T'_{\mathrm{r,p}} = \frac{S}{z'_{\mathrm{p}}} = \frac{S}{S + \ln 2} > 0.5 \tag{27}$$

or $S > 0.69$. In other words, if $S < 0.69$, then the minimum value of $g(z_{\mathrm{p}})$ would fall well below the nucleation regime. Hence, it appears that for those inorganic materials which exhibit normal crystal growth one can anticipate that the density of nucleated particles will indeed increase with T_{p}^{-1}.

Furthermore, it should be noted that many of the glassy systems which nucleate homogeneously do not obey a normal crystal growth law, but a screw dislocation growth mechanism, as lithium disilacate glass [28], and for this type of mechanism the sign of the function $[\mathrm{d}^2(\ln H_{1\mathrm{p}})]/\mathrm{d}T_{\mathrm{p}}^2$ must be analyzed. Aside from a constant factor, which may be ignored, one has

$$H_1 = (\Delta T)H \tag{28}$$

where H_1 and H, are the temperature-dependent terms in the growth rate expressions for screw dislocation and normal growth, respectively, and $\Delta T = T_{\mathrm{m}} - T$. Taking the second derivative of the logarithmic form of Eq. (28) with respect to T_{p}, bearing in mind Eq. (23), and substituting Eq. (28) into the resulting expression, one obtains

$$\begin{aligned} &H_{1\mathrm{p}}\frac{\mathrm{d}^2H_{1\mathrm{p}}}{\mathrm{d}T_{\mathrm{p}}^2} - \left(\frac{\mathrm{d}H_{1\mathrm{p}}}{\mathrm{d}T_{\mathrm{p}}}\right)^2 \\ &\quad = (\Delta T_{\mathrm{p}})^2\left[H_{\mathrm{p}}\frac{\mathrm{d}^2H_{\mathrm{p}}}{\mathrm{d}T_{\mathrm{p}}^2} - \left(\frac{\mathrm{d}H_{\mathrm{p}}}{\mathrm{d}T_{\mathrm{p}}}\right)^2\right] - H_{\mathrm{p}}^2 \end{aligned} \tag{29}$$

which, according to Eq. (23), may be rewritten as

$$H_{1\mathrm{p}}^2\frac{\mathrm{d}^2(\ln H_{1\mathrm{p}})}{\mathrm{d}T_{\mathrm{p}}^2} = H_{\mathrm{p}}^2\left[(\Delta T_{\mathrm{p}})^2\frac{\mathrm{d}^2(\ln H_{\mathrm{p}})}{\mathrm{d}T_{\mathrm{p}}^2} - 1\right] \tag{30}$$

and given that the term $[\mathrm{d}^2(\ln H_{\mathrm{p}})]/\mathrm{d}T_{\mathrm{p}}^2$ has been proved to be negative, then it follows that $[\mathrm{d}^2(\ln H_{1\mathrm{p}})]/\mathrm{d}T_{\mathrm{p}}^2 < 0$ and therefore the term $A_2 < 0$ for a screw dislocation growth mechanism.

Finally, as a summary of the present analysis one may affirm that the materials with normal crystal growth or screw dislocation growth, which fulfill the appointed conditions, verify $\mathrm{d}r/\mathrm{d}T_{\mathrm{p}} < 0$, accordingly $\mathrm{d}N/\mathrm{d}T_{\mathrm{p}}^{-1} > 0$ and, therefore, the density of nucleated particles will increase with increasing T_{p}^{-1}.

2.2. A study on the variation in N with $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$

It is pointed out in the literature [9] that the quantity $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ increases with the number of particles nucleated. Therefore, it is interesting to research if this fact is a general result of merely a consequence of the specific systems, which have been studied.

First, the behavior of $x(T_{\mathrm{p}}) = x_{\mathrm{p}}$ will be analyzed as T_{p} increases. This result will be used in subsequent studies. By considering bulk crystallization and $T = T_{\mathrm{p}}$, Eq. (5) becomes

$$h(x_{\mathrm{p}}) = [-\ln(1-x_{\mathrm{p}})]^{1/3} = \left(\frac{4\pi}{3}\right)^{1/3} r\int_{T_0}^{T_{\mathrm{p}}} u(T)\,\mathrm{d}T \tag{31}$$

Taking the derivative of Eq. (31) with respect to T_{p}, and assuming that T_{p} depends on r, gives

$$\frac{\mathrm{d}x_{\mathrm{p}}}{\mathrm{d}T_{\mathrm{p}}} = \left(\frac{4\pi}{3}\right)^{1/3}\left[\frac{\mathrm{d}h(x_{\mathrm{p}})}{\mathrm{d}x_{\mathrm{p}}}\right]^{-1}\left[I_{\mathrm{p}}\frac{\mathrm{d}r}{\mathrm{d}T_{\mathrm{p}}} + ru(T_{\mathrm{p}})\right] \tag{32}$$

If one substitutes into Eq. (32) the expression of $\mathrm{d}r/\mathrm{d}T_{\mathrm{p}}$, given in Eq. (15), one obtains

$$\begin{aligned} \frac{\mathrm{d}x_{\mathrm{p}}}{\mathrm{d}T_{\mathrm{p}}} &= (36\pi)^{-2/3}\left[\frac{\mathrm{d}h(x_{\mathrm{p}})}{\mathrm{d}x_{\mathrm{p}}}\right]^{-1}\frac{1}{\beta r^2 I_{\mathrm{p}}^2} \\ &\quad\times\left[\left(1 - \frac{\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}^2}\frac{I_{\mathrm{p}}}{\beta}\right)\frac{\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}} + \left(\ddot{u}_{\mathrm{p}} - \frac{\dot{u}_{\mathrm{p}}^2}{u_{\mathrm{p}}}\right)\frac{I_{\mathrm{p}}}{\beta u_{\mathrm{p}}^2}\right] \end{aligned} \tag{33}$$

It should be noted that, as it has been demonstrated in Section 2.1, the second term in the square brackets on the right side of Eq. (33) is always negative (for normal or screw dislocation growth). Regarding the first term in the brackets one substitutes into the quoted term the expression of $\dot{u}_{\mathrm{p}}I_{\mathrm{p}}/\beta u_{\mathrm{p}}^2$ given in Eq. (14) and considering Eq. (31), one has

$$\begin{aligned} \frac{\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}}\left(1 - \frac{\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}^2}\frac{I_{\mathrm{p}}}{\beta}\right) &= \frac{3\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}}\left[1 - \frac{4\pi}{3}(rI_{\mathrm{p}})^3\right] \\ &= \frac{3\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}}[1 - h^3(x_{\mathrm{p}})] \end{aligned} \tag{34}$$

By analyzing the sign of Eq. (33) it is clear that $\mathrm{d}x_{\mathrm{p}}/\mathrm{d}T_{\mathrm{p}} < 0$ when $\dot{u}_{\mathrm{p}} < 0$. However, for $\dot{u}_{\mathrm{p}} > 0$, the algebraic sign of the first term in the square brackets of Eq. (33) depends on whether $h(x_{\mathrm{p}})$ is greater than or less than unity, according to Eq. (34). By considering Eq. (6) and the relationship $\mathrm{d}N/\mathrm{d}T_{\mathrm{p}}^{-1} > 0$ it is clear that x_{p} is a decreasing function of T_{p} (i.e., an increasing function of r) in order to show that $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ increases as the parameter r increases. By means of considerations of Eqs. (33) and (34), it will be demonstrated that $h(x)$ can never exceed unity for any T_{p} values, regardless of whether or not $\mathrm{d}x_{\mathrm{p}}/\mathrm{d}T_{\mathrm{p}} < 0$. First, it must be considered the smallest possible value of T_{p} (i.e., $T_{\mathrm{p}} \to T_0$) and taking limits in Eq. (34),yields

$$\begin{aligned} &3\left\{1 - \left[\lim_{T_{\mathrm{p}}\to T_0}(h(T_{\mathrm{p}}))\right]^3\right\} \\ &\quad = 1 - \frac{1}{\beta}\left(\lim_{T_{\mathrm{p}}\to T_0}\frac{I_{\mathrm{p}}}{u_{\mathrm{p}}}\right)\left(\lim_{T_{\mathrm{p}}\to T_0}\frac{\dot{u}_{\mathrm{p}}}{u_{\mathrm{p}}}\right) \end{aligned} \tag{35}$$

bearing in mind that for sufficiently small T_0, $u(T_0) \to 0$, then, by using L'Hospital's rule, one obtains

$$\lim_{T_{\mathrm{p}}\to T_0}\frac{I_{\mathrm{p}}}{u_{\mathrm{p}}} = \beta\lim_{T_{\mathrm{p}}\to T_0}\frac{u_{\mathrm{p}}}{\dot{u}_{\mathrm{p}}}$$

and according to Eq. (35), $\lim_{T_p \to T_0} [h(T_p)] = 1$. Thus, $h(x)$ initially does not exceed unity. Hence, $1 - h(x_p)$ is initially zero, and considering Eq. (33), dx_p/dT_p is negative initially. Since $h(x_p)$ decreases as x_p decreases and bearing in mind the above-mentioned decrease of x_p with the increase of T_p it is clear that $h(x_p)$ will become less than unity. Therefore, $h(x_p)$ has a maximum value of unity, and according to Eq. (31) the largest value of x_p is $1 - e^{-1} \approx 0.632$. Once having established that $h(x_p) \leq 1$, it is relatively simple to demonstrate that $(dx/dt)|_p$ must increase with r. Taking the derivative of Eq. (31) with respect to an arbitrary T, then one finds

$$\frac{dx}{dT} = \left(\frac{4\pi}{3}\right)^{1/3} \frac{ru}{h'} \quad \text{with } h' \equiv \frac{dh(x)}{dx}$$

or

$$\dot{x} = \frac{dx}{dt} = \left(\frac{4\pi}{3}\right)^{1/3} \beta \frac{ru}{h'} \tag{36}$$

Now by considering Eq. (36) for $T = T_p$, allowing T_p to be a function of r, and taking the derivative of Eq. (36) with respect to r, one obtains

$$\frac{d\dot{x}_p}{dr} = \left(\frac{4\pi}{3}\right)^{1/3} \left\{ \frac{\beta u_p}{h'} + \left[\frac{r\dot{u}_p}{h'} - \frac{ru_p h''}{h'^2} \frac{dx_p}{dt} \right] \frac{dT_p}{dr} \right\} \tag{37}$$

By substituting into Eq. (37) the value of dx_p/dt given in Eq. (32), yields

$$\begin{aligned} \frac{d\dot{x}_p}{dr} = \left(\frac{4\pi}{3}\right)^{1/3} \Bigg\{ \frac{\beta u_p}{h'} + \Bigg[\frac{r\dot{u}_p}{h'} - \left(\frac{4\pi}{3}\right)^{1/3} \\ \times \beta \frac{ru_p h''}{h'^3} \left(I_p \frac{dr}{dT_p} + ru_p \right) \Bigg] \frac{dT_p}{dr} \Bigg\} \end{aligned} \tag{38}$$

Moreover, the maximum crystallization rate is found by making $d^2x/dt^2 = 0$, and, therefore, taking the derivative of Eq. (36) with respect to time and making $T = T_p$ leads to

$$h'' = \frac{d^2h}{dx^2} = \frac{h'^2 \dot{u}_p}{(4\pi/3)^{1/3} \beta r u_p^2} \tag{39}$$

If this expression of h'' is substituted in Eq. (38) one may write that

$$\frac{d\dot{x}_p}{dr} = 3 \left(\frac{4\pi}{3}\right)^{1/3} \beta \frac{u_p}{h'} [1 - h^3(x_p)] \tag{40}$$

Since $h' > 0$ for all T_p, and it has been shown that $1 - h^3(x_p) > 0$, then $d\dot{x}_p/dr > 0$, the result which was to be demonstrated. Thus, it has been demonstrated that one expects $(dx/dt)|_p$ to be an increasing function of N for most systems. By considering bulk crystallization and taking the derivative of Eq. (5) with respect to time for $T = T_p$ gives a relationship between $(dx/dt)|_p$ and r of which logarithmic form one may write as

$$\begin{aligned} \ln (dx/dt)|_p = \ln 4\pi\beta + 3 \ln r + \ln u_p + 2 \ln \int_{T_0}^{T_p} u(T)\, dT \\ - \frac{4\pi}{3} \left[r \int_{T_0}^{T_p} u(T)\, dT \right]^3 \end{aligned} \tag{41}$$

If one substitutes into Eq. (41) the value of the term $[r\int_{T_0}^{T_p} u(T)\, dT]^3$, given in Eq. (14), the following relationship is obtained

$$\begin{aligned} \ln \left(\frac{dx}{dt}\right)\Bigg|_p = \ln 4\pi - 2 \ln \beta + 3 \ln N + \ln u_p + 2 \ln I_p \\ - \frac{1}{3} \left(2 + \frac{\dot{u}_p I_p}{\beta u_p^2} \right) \end{aligned} \tag{42}$$

where it should be noted that $\ln(dx/dt)|_p$ is a function of the logarithm of the density of nuclei.

3. Justifying by an example the variations in N with T_p^{-1} and $(dx/dt)|_p$

Although Eq. (13) predicts a linear increase of the logarithm of the density of nucleated particles with T_p^{-1}, however, from an inspection of Eq. (14), such a simple relationship is not at all apparent. In order to assess the dependence of N upon T_p^{-1}, Eq. (14) has been applied to the nucleation and crystallization of $Li_2O{\cdot}2SiO_2$ glass in the temperature region quoted in the literature [9]. In this sense, the logarithmic form of Eq. (14) may be written in the explicit form of $\ln N$ as

$$\ln N = \ln \beta - \frac{1}{3} \ln 4\pi - \ln I_p + \frac{1}{3} \ln \left[2 - \frac{d(u^{-1})}{dT}\Bigg|_p I_p \right] \tag{43}$$

By considering the maximum peak temperature, T_{1p}, for samples nucleated at identical temperature, but different times, the logarithm of the density of nucleated particles (normalized) can be expressed as

$$\ln \left(\frac{\mathrm{N}}{N_1}\right) = \ln(I_{1p}/I_p) + \frac{1}{3} \ln \frac{2 - [d(u^{-1})/dT]|_p I_p}{2 - [d(u^{-1})/dT]|_{1p} I_{1p}} \tag{44}$$

where $N_1$and I_{1p} are, respectively, the values of N and I_p for above-mentioned maximum peak temperature.

Bearing in mind Eq. (20) where the viscosity, η, is of Fulcher form and H is a function of temperature given by Eq. (22), one obtains

$$\begin{aligned} I_p = u_0 \int_{T_0}^{T_p} \eta^{-1} H\, dT = u_0 e^{-\alpha} \int_{T_0}^{T_p} e^{-\gamma/(T-T_0)} (1 - Ae^{-BT}) \\ dT = u_0 e^{-\alpha} (I_1 - AI_2) \end{aligned} \tag{45}$$

If it is assumed that $T_0 \ll T$, $T - T_0 \approx T$, then the integral I_2 becomes

$$I_2=\int_{T_0}^{T_\mathrm{p}} \mathrm{e}^{-(\gamma+B)/(T-T_0)}\,\mathrm{d}T$$

By using the substitutions $y_1 = \gamma/(T - T_0)$ and $y_2 = (\gamma + B)/(T - T_0)$, and by considering Eq. (10) with the restrictions imposed to this equation, the integrals I_1 and I_2 can be written as

$$I_1=\frac{(T_\mathrm{p}-T_0)^2}{\gamma}\exp\left[\frac{-\gamma}{T_\mathrm{p}-T_0}\right]$$

and

$$I_2=\frac{(T_\mathrm{p}-T_0)^2}{\gamma+B}\exp\left[\frac{-(\gamma+B)}{T_\mathrm{p}-T_0}\right],$$

respectively, and accordingly Eq. (45) becomes

$$\begin{aligned} I_\mathrm{p}&=u_0\mathrm{e}^{-\alpha}(T_\mathrm{p}-T_0)^2\\ &\quad\times\left\{\frac{1}{\gamma}\exp\left[\frac{-\gamma}{T_\mathrm{p}-T_0}\right]-\frac{A}{\gamma+B}\exp\left[\frac{-(\gamma+B)}{T_\mathrm{p}-T_0}\right]\right\}\\ &=u_0\mathrm{e}^{-\alpha}(T_\mathrm{p}-T_0)^2(F_\mathrm{p}-G_\mathrm{p}),\quad \text{with}\\ G_\mathrm{p}&=\frac{A}{\gamma+B}\exp\left[\frac{-(\gamma+B)}{T_\mathrm{p}-T_0}\right] \end{aligned}\tag{46}$$

On the other hand, by considering the reciprocal quantity of crystal growth rate, $u^{-1} = u_0^{-1}\eta H^{-1}$, the term $\mathrm{d}(u^{-1})/\mathrm{d}T$ is written as

$$\frac{\mathrm{d}(u^{-1})}{\mathrm{d}T}=u_0^{-1}H^{-1}\left(\frac{\mathrm{d}\eta}{\mathrm{d}T}-\eta H^{-1}\frac{\mathrm{d}H}{\mathrm{d}T}\right)$$

and bearing in mind the above-mentioned Fulcher form for the viscosity and the function H given by Eq. (22), the last expression becomes

$$\left.\frac{\mathrm{d}(u^{-1})}{\mathrm{d}T}\right|_\mathrm{p}=u_0^{-1}\eta_\mathrm{p}H_\mathrm{p}^{-1}(T_\mathrm{p}-T_0)^{-2}[-\gamma+B(H_\mathrm{p}^{-1}-1)]$$

thus the product $[\mathrm{d}(u^{-1})/\mathrm{d}T]|_\mathrm{p}I_\mathrm{p}$ in Eq. (44) can be expressed as

$$\begin{aligned}\left.\frac{\mathrm{d}(u^{-1})}{\mathrm{d}T}\right|_\mathrm{p}I_\mathrm{p}&=\mathrm{e}^{\gamma/(T_\mathrm{p}-T_0)}H_\mathrm{p}^{-1}\\ &\quad\times[-\gamma+B(H_\mathrm{p}^{-1}-1)](F_\mathrm{p}-G_\mathrm{p})\end{aligned}\tag{47}$$

According to Eqs. (22) and (46) if B is large $H_\mathrm{p}^{-1}\approx 1$, therefore $-\gamma+B(H_\mathrm{p}^{-1}-1)\approx-\gamma$ and $F_\mathrm{p}\gg G_\mathrm{p}$, which entails $F_\mathrm{p}-G_\mathrm{p}\approx F_\mathrm{p}$ and accordingly $[\mathrm{d}(u^{-1})/\mathrm{d}T]_\mathrm{p}I_\mathrm{p}=-1$. Bearing in mind this fact, the second term on the right side of Eq. (44) is zero, and according to Eq. (46) the logarithm of the density of nucleated particles (normalized) is written as

$$\begin{aligned}\ln\left(\frac{\mathrm{N}}{N_1}\right)&=2\ln\frac{T_{1\mathrm{p}}-T_0}{T_\mathrm{p}-T_0}\\ &\quad+\gamma[(T_\mathrm{p}-T_0)^{-1}-(T_{1\mathrm{p}}-T_0)^{-1}]\end{aligned}\tag{48}$$

This expression, obtained from Eq. (14), allows to evaluate $\ln(N/N_1)$ for different peak temperatures and by means of a representation $\ln(N/N_1)$ versus the reciprocal of reduced peak temperature to verify the variation in N with T_p^{-1}.

Also it is possible to assesses the dependence of N upon $(\mathrm{d}x/\mathrm{d}t)|_\mathrm{p}$ In this sense, if the density of nuclei, N_2, corresponds to a maximum peak temperature, $T_{2\mathrm{p}}$, according to Eq. (42), the logarithm of the maximum crystallization rate (normalized) can be written as

$$\begin{aligned}\ln\frac{(\mathrm{d}x/\mathrm{d}t)|_\mathrm{p}}{(\mathrm{d}x/\mathrm{d}t)|_{2\mathrm{p}}}&=3\ln\frac{N}{N_2}+\ln\frac{u_\mathrm{p}}{u_{2\mathrm{p}}}+2\ln\frac{I_\mathrm{p}}{I_{2\mathrm{p}}}\\ &\quad-\frac{1}{3\beta}\left(\frac{\dot{u}_\mathrm{p}I_\mathrm{p}}{u_\mathrm{p}^2}-\frac{\dot{u}_{2\mathrm{p}}I_{2\mathrm{p}}}{u_{2\mathrm{p}}^2}\right)\end{aligned}\tag{49}$$

Bearing in mind Eq. (20), the above quoted expressions of the functions $\eta(T)$, and $H(T)$ and the hypothesis of large B, the term $\ln(u_\mathrm{p}/u_{2\mathrm{p}})$ of Eq. (49) becomes

$$\ln\frac{u_\mathrm{p}}{u_{2\mathrm{p}}}=\gamma[(T_{2\mathrm{p}}-T_0)^{-1}-(T_\mathrm{p}-T_0)^{-1}]\tag{50}$$

Moreover, according to Eq. (46), the third term of Eq. (49) is written as

$$\begin{aligned}2\ln\frac{I_\mathrm{p}}{I_{2\mathrm{p}}}&=2\ln\frac{(T_\mathrm{p}-T_0)^2F_\mathrm{p}}{(T_{2\mathrm{p}}-T_0)^2F_{2\mathrm{p}}}\\ &=4\ln\frac{T_\mathrm{p}-T_0}{T_{2\mathrm{p}}-T_0}+2\gamma[(T_{2\mathrm{p}}-T_0)^{-1}-(T_\mathrm{p}-T_0)^{-1}]\end{aligned}\tag{51}$$

On the other hand, given that $\dot{u}=\mathrm{d}u/\mathrm{d}t=-u^2\,\mathrm{d}(u^{-1})/\mathrm{d}t$, the term $\dot{u}_\mathrm{p}I_\mathrm{p}/\beta u_\mathrm{p}^2$ of Eq. (49) can be expressed as

$$\frac{\dot{u}_\mathrm{p}I_\mathrm{p}}{\beta u_\mathrm{p}^2}=-I_\mathrm{p}\left.\frac{\mathrm{d}(u^{-1})}{\mathrm{d}T}\right|_\mathrm{p}$$

and considering Eq. (47), if B is large (above-mentioned hypothesis) the fourth term on the right side of Eq. (49) is zero, according to the following expression

$$\begin{aligned}&\frac{1}{3\beta}\left(\frac{\dot{u}_\mathrm{p}I_\mathrm{p}}{u_\mathrm{p}^2}-\frac{\dot{u}_{2\mathrm{p}}I_{2\mathrm{p}}}{u_{2\mathrm{p}}^2}\right)\\ &\quad=\frac{1}{3}\gamma[\mathrm{e}^{\gamma/(T_\mathrm{p}-T_0)}F_\mathrm{p}-\mathrm{e}^{\gamma/(T_{2\mathrm{p}}-T_0)}F_{2\mathrm{p}}]=0\end{aligned}\tag{52}$$

Finally, bearing in mind Eqs. (50)–(52) the logarithm of the maximum crystallization rate (normalized) becomes

$$\begin{aligned}\ln\frac{(\mathrm{d}x/\mathrm{d}t)|_\mathrm{p}}{(\mathrm{d}x/\mathrm{d}t)|_{2\mathrm{p}}}&=3\ln\frac{N}{N_2}+3\gamma[(T_{2\mathrm{p}}-T_0)^{-1}-(T_\mathrm{p}-T_0)^{-1}]\\ &\quad+4\ln\frac{T_\mathrm{p}-T_0}{T_{2\mathrm{p}}-T_0}\end{aligned}\tag{53}$$

when the B parameter is large. This expression, obtained from Eq. (14), permits to evaluate $\ln[(\mathrm{d}x/\mathrm{d}t)|_\mathrm{p}/(\mathrm{d}x/\mathrm{d}t)|_{2\mathrm{p}}]$ for different peak temperatures and by means of a representation of logarithm of the maximum crystallization rate

Table 1
Values normalized corresponding to the functions $\ln N$ and $\ln\,(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ for $\mathrm{LiO_2{\cdot}2SiO_2}$ glass, calculated from the peak temperatures, by using Eqs. (48) and (53), respectively

Variation in N with T_{r}^{-1}			Variation in N with $(\mathrm{d}x/\mathrm{d}t)\|_{\mathrm{p}}$			
T_{p} (K)	T_{r}^{-1}	$\ln(N/N_1)$	T_{p} (K)	T_{r}^{-1}	$\ln(N/N_2)$	$\ln\frac{(\mathrm{d}x/\mathrm{d}t)\|_{\mathrm{p}}}{(\mathrm{d}x/\mathrm{d}t)\|_{2\mathrm{p}}}$
958.0	1.3644	0	918.0	1.4237	0	0
953.1	1.3713	0.07796	911.4	1.4341	0.12828	0.04129
948.1	1.3785	0.15934	904.8	1.4445	0.26114	0.08346
943.3	1.3856	0.23929	898.2	1.4551	0.39885	0.12651
938.2	1.3932	0.32626	891.7	1.4657	0.53952	0.16986
933.1	1.4008	0.41541	885.0	1.4768	0.69009	0.21554
928.1	1.4082	0.50501	878.6	1.4876	0.83954	0.26016
922.9	1.4163	0.60060	872.0	1.4989	0.99981	0.30728

(normalized) versus $\ln(N/N_2)$, also to verify the variation in N with $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$.

With the aim of representing the above-mentioned variations in N with T_{p}^{-1} and $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$, the data corresponding for the viscosity of Fulcher form and for the function of temperature, H, of the $\mathrm{Li_2O{\cdot}2SiO_2}$ glass have been taken from the literature [9], namely: $\alpha = 1.81$, $\gamma = 1347$ for the viscosity; $A = \mathrm{e}^{5.27}$ and $B = 5.27T_{\mathrm{m}}$ ($T_{\mathrm{m}} = 1307\,\mathrm{K}$) for the function H. Also, the initial temperature of the process, $T_0 = 595\,\mathrm{K}$, and two sets of peak temperatures, which appear in Table 1, were taken from the literature [9]. By using the above-mentioned data and by means of Eqs. (48) and (53) the corresponding values of $\ln(N/N_1)$ and $\ln[(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}/(\mathrm{d}x/\mathrm{d}t)|_{2\mathrm{p}}]$, shown in Table 1,were calculated. Moreover, the reciprocal values of the reduced peak temperatures are also listed in the quoted Table 1. The data of the logarithm of the density of nucleated particles (normalized) are plotted against the reciprocal of the reduced peak temperatures in Fig. 2. It is observed that $\ln(N/N_1)$ can be represented as a linear function of T_{p}^{-1} to a good approximation. The corresponding regression straight line has the following equation

$$\ln\left(\frac{N}{N_1}\right) = \frac{11.5641}{T_{\mathrm{r}}} - 15.7812$$

with a correlation coefficient $r = 0.9991$. Thus, the linear variation in N with T_{p}^{-1} appears to be justified for the study of the nucleation behavior of lithium disilicate. It is important to note that the present conclusion has been drawn without making the usual and unjustified assumption that $u(T)$ is of Arrhenius type.

On the other hand, the logarithm of the maximum crystallization rate is plotted as a function of the logarithm of the density of nuclei, both normalized, in Fig. 3. It should be noted that a nearly linear relationship is obtained, which has the following equation

$$\ln\frac{(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}}{(\mathrm{d}x/\mathrm{d}t)|_{2\mathrm{p}}} = 0.3074\ln\left(\frac{\mathrm{N}}{N_2}\right) + 2.3178\times10^{-3}$$

with a correlation coefficient $r = 0.9998$. This fact demonstrates that a linear variation in $\ln N$ with $\ln(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ also

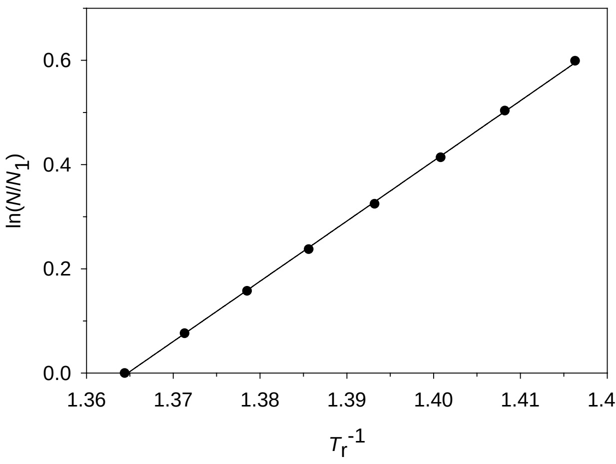

Fig. 2. Plot of the logarithm of the density of nucleated particles (normalized) vs. reciprocal of the reduced peak temperature and the corresponding regression straight line for $\mathrm{Li_2O{\cdot}2SiO_2}$ glass. N_1 is the density of nuclei corresponding to a peak temperature of 958 K. The values of $\ln(N/N_1)$ have calculated by using Eq. (48).

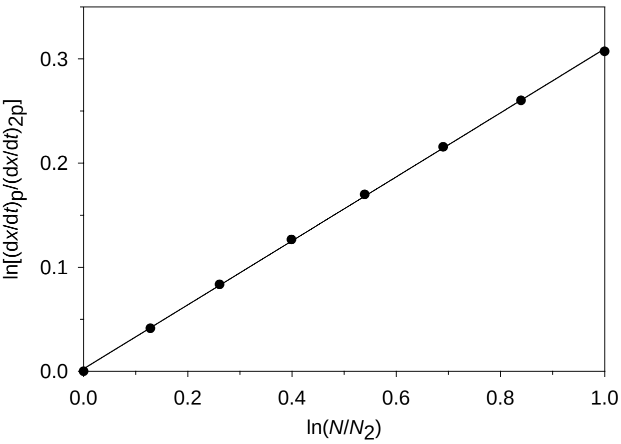

Fig. 3. Plot of the logarithm of the maximum crystallization rate vs. the logarithm of the density of nucleated particles, both normalized, and the corresponding regression straight line for the lithium disilicate glass. N_2 is the density of nuclei corresponding to a peak temperature of 918 K. The values of $\ln[(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}/(\mathrm{d}x/\mathrm{d}t)|_{2\mathrm{p}})]$ have been calculated by using Eq. (53).

appears to be adequated for the analysis of the nucleation process of $Li_2O{\cdot}2SiO_2$ glass.

4. Conclusions

The present work considers the use of DSC experiments for the determination of the temperature dependence of homogeneous crystal nucleation rates of glassy solids. The variations in the density of nuclei both with the reciprocal of the peak temperature and with the maximum crystallization rate, which has been employed for this purpose, were analyzed.

The variation in N with T_p^{-1} is based upon the increase in the density of nuclei with the reciprocal of peak temperature. Its use had been justified in the last decades by arguments which did not consider realistic expressions for the temperature dependence of the crystal growth rate. Herein, it has been demonstrated for two standard crystal growth models, normal and screw dislocation growth, that the density of nuclei will increase with T_p^{-1} in most systems. Furthermore, the growth model appropriate for lithium disilicate crystal growth, was used to find the change in N with T_p^{-1}. A linear relationship between $\ln N$ and T_p^{-1} was found to be a good approximation for $N = f_1\ (T_p^{-1})$ for $LiO_2{\cdot}2SiO_2$ nucleation.

The variation in N with $(dx/dt)|_p$, according to literature [9], is based upon the observation that the maximum crystallization rate increases with the density of nucleated particles. In the present work, it was shown that $(dx/dt)|_p$ is expected to increase with N for glassy systems which exhibit normal or screw dislocation growth. Also, calculations performed for nucleation of $Li_2O{\cdot}2SiO_2$ glass indicate that a linear relationship there is between the logarithm forms of $(dx/dt)|_p$ and N.

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