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## Crystal nucleation and growth kinetics of NaF in photo-thermo-refractive glass

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### Abstract

Photo-thermo-refractive (PTR) glass is an optically transparent photosensitive oxide glass. Upon heating, the UV-exposed regions of this glass undergo copious crystallization of NaF nano-crystals giving rise to a permanent, localized refractive index change. But the unexposed parts of the glass also undergo some crystallization which causes unwanted light scattering. Holographic optical elements produced from PTR glass have been used in special laser systems. In this article we report, for the first time since the invention of PTR glass about half-century ago, the steady-state nucleation rates, nucleation time-lags and crystal growth rates for UV-unexposed PTR glass estimated in a wide temperature range, from  $T_g \sim 470^\circ\text{C}$  up to  $750^\circ\text{C}$ . A self-consistent description of these data is presented in the framework of CNT using the interfacial free energy of the critical nuclei and the effective diffusion coefficient as adjustable parameters. The diffusivity calculated from crystallization kinetics and that estimated from viscous flow via the Stokes-Einstein-Eyring equation show a decoupling phenomenon.

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## 1. Introduction

Photo-thermo-refractive (PTR) glass is a Si-Na-Al-Zn-Br-F oxide glass doped with Ce, Ag, Sb and Sn. Upon heating, the UV-exposed regions of this photosensitive glass undergo copious crystallization of NaF nano-crystals, giving rise to a permanent, localized refractive index change. Holographic optical elements produced from this optically transparent glass have been increasingly used in special laser systems.

Unfortunately, the un-exposed regions of PTR glass also undergo crystallization upon adequate heat treatment, but the number of crystals is larger in the UV-exposed regions [1]. The significance of knowing the detailed crystal nucleation and growth kinetics in both UV-exposed and un-exposed PTR glass stems from the fact that these kinetic parameters help to design proper thermal treatments to reach the wanted degree of crystallinity and crystal size distribution in order to achieve the desired optical effect (localized, permanent refractive index change) and, at the same time, to optimize optical transmission and to minimize light scattering.

The study of the crystallization kinetics of NaF in PTR glass has not only practical but also theoretical importance, since PTR glass provides a good model for analyzing processes of nucleation and growth of a minor phase, in this case of sodium fluoride, i.e. when a strong difference between the compositions of the parent glass and the precipitated crystalline phase takes place. In this case (at least in the advanced stages of the phase transformation) crystal growth is accompanied by the formation of diffusion zones that are depleted in fluoride and sodium and changes in the composition of the residual liquid [2]. The thermodynamic driving force for such type of crystallization is the supersaturation of the melt with respect to the dissolved phase, which, in this case, is crystalline NaF. At any given temperature, the thermodynamic driving force changes with time during crystallization becoming null when the NaF crystal volume fraction approaches the equilibrium value. By estimating the equilibrium volume fraction of NaF crystals, its solubility in PTR glass was estimated as a function of temperature [3]. It was shown in ref. [4] that the presence of KBr reduces the solubility of the NaF crystals. This finding has clarified the role of bromine on the NaF crystallization in PTR glass. Moreover, liquid-liquid phase separation in PTR glass was first investigated and reported in ref. [5].

Over 100 papers have been published worldwide with the keywords “photo thermo refractive glass” since 1999. The present paper is a logical continuation of these and our own

long-standing systematic investigations intended to unveil the intricate *crystallization* process of PTR glass. In addition to the effects analyzed by us and briefly mentioned above [2-5], in ref. [1] we have also studied already the overall crystallization kinetics of PTR glass by DSC methods. The present research is aimed at the (difficult to perform) *direct measurement* of nucleation rates, time-lags and growth rates of NaF crystals in UV-un-exposed PTR glass as a function of temperature, and their analysis in the framework of classical nucleation theory (CNT).

## 2. Material and Methods

A classical PTR glass with composition 15Na<sub>2</sub>O–5ZnO–4Al<sub>2</sub>O<sub>3</sub>–70SiO<sub>2</sub>–5NaF–1KBr–0.01Ag<sub>2</sub>O–0.01CeO–0.01SnO<sub>2</sub>–0.03Sb<sub>2</sub>O<sub>3</sub> (mol%) was melted at 1460°C in a platinum crucible, in air, and stirred for 5 h. Annealing was carried out at 460°C for 1 h followed by cooling to room temperature at 0.1 K/min. Thus the resulting glass had already an extensive low temperature pre-history. We investigated the crystallization kinetics at higher temperatures beginning with the glass transition temperature  $T_g=470^\circ\text{C}$  up to  $T=750^\circ\text{C}$ .

The nucleation rate,  $I$ , is generally defined as

$$I = dN_v / dt, \quad (1)$$

where  $N_v$  is the number of supercritical crystals per unit volume and  $t$  is the time of nucleation. Hence, to estimate the nucleation rate at any given temperature one needs to know  $N_v$  as a function of nucleation time. The main problem in the experimental determination of  $I$  is, as a rule, the extremely small size of the crystals (only a few tens of Angstroms) nucleated and grown at any nucleation temperature,  $T_n$ . In order to reach a detectable nucleation rate, the undercoolings have to be sufficiently high. Due to the increase of the viscosity or the decrease of the effective diffusion coefficients with decreasing temperature, the crystal growth rates  $U(T_n)$  at nucleation temperatures are often too small to allow the crystallites to grow to measurable sizes in reasonable experimental time scales. To overcome this problem we used the so called “development” method, proposed more than a hundred years ago by G. Tammann [6]. This method is frequently employed in nucleation studies. According to this technique, the crystals nucleated at  $T_n$  are grown at a higher temperature  $T_d > T_n$  up to a size detectable in a light or electron microscope. The development temperature,  $T_d$ , has to satisfy the following conditions:

$$U(T_d) \gg U(T_n), \quad I(T_d) \ll I(T_n). \quad (2)$$

It should be noted (cf. also [7]), however, that not all crystals formed at  $T_n$  can develop at  $T_d$ , but only those grown at  $T_n$  up to a size larger than the critical size,  $R_d^*$ , corresponding to the critical cluster size at the development temperature,  $T_d > T_n$ . Recall that the critical size increases with temperature as we will shown below. One can find more details about the “development” method in ref. [7, 8].

A very special problem in the analysis of nucleation rates in the case of PTR glass is the determination of the crystal number density,  $N_V$ . The dendritic shape of the crystals at  $T_d$ , and the very high values of  $N_V$  of the PTR glass samples strongly complicate the application of the standard stereological methods. Therefore, here we elaborated and used an approximate, fast, little material demanding method that gives reasonable, reproducible results. Small (100-500 $\mu\text{m}$ ) bits were prepared from heat-treated glass samples (chipped directly onto a transparent glass slide). Then the average distances,  $L$ , between the crystal centers were estimated using transmitted or reflected light microscopy. It should be noted that in the case of transmitted light, due to the small depth of field, most of the observed crystals located within a very thin layer of the sample. The following approximate equation relates  $L$  with the average crystal number density  $N_V$ ,

$$N_V = L^{-3}. \quad (3)$$

The crystal growth rates were estimated by the standard procedure via crystal size *vs.* time plots.

### 3. Experimental results

A typical  $N_V^d$  *versus* nucleation time plot for the system under consideration is shown in **Fig.1**. The superscript  $d$  denotes that this number density was obtained by the “development” method. The unusual (as compared with classical cases), non-monotonic growth of the  $N_V^d(t)$ -curve will be discussed later. **Fig. 2** shows an example of NaF crystals grown at a relatively high temperature close to that employed for crystal development. Dendrite-like crystals have an approximately spherical external form, which we characterized by its maximal size ( $2R$ ). **Fig.3** shows one of the plots of crystal size  $R$  (“radius”) *versus* growth time. To estimate the crystal

growth rate  $U = dR / dt$  we used only the initial part of the  $R(t)$ -plot. The decrease of  $U$  during the advanced stage of phase transition will be commented later in the discussion.

The values of  $U(T)$  measured by the above described method are collected in **Table 1** and plotted in **Fig.4** for different temperatures.

#### 4. Treatment of the experimental data

As was noted in Section 2 not all crystals nucleated at  $T_n$  can be grown-up to detectable sizes at  $T_d > T_n$  due to the following considerations. The critical crystal size is given by Eq.(4)

$$R^* = \frac{2\sigma}{\Delta G_V} . \quad (4)$$

Here  $\sigma$  (J/m<sup>2</sup>) is the specific energy of the melt/critical crystal interface and  $\Delta G_V$  (J/m<sup>3</sup>) is the thermodynamic driving force for crystallization. The critical crystal size increases with temperature, mainly due to the decrease of  $\Delta G_V$ . Hence all the crystals having sizes between the critical sizes  $R_n^*$  and  $R_d^*$ , corresponding to nucleation and “development” temperatures, respectively, dissolve at  $T_d$ . This dissolution effect results in a shift of the  $N_V^d(T_n, T_d) \sim t$  curve estimated by the “development” method relative to the  $N_V(T_n) \sim t$  curve, by a time  $t_o$  needed for the increase of cluster size from  $R_n^*$  to  $R_d^*$ , in such a way that

$$N_V(T_n, t) = N_V^d(T_n, (t - t_o)) . \quad (5)$$

One can find more details about the development method in refs. [8, 9, 10, 11]. Thus, the crystals of the above described size interval must grow at  $T_n$  up to a size  $R > R_d^*$  to be developed at  $T_d$ .

Two groups of crystals can be distinguished with respect to their formation conditions. The *first* group includes the crystals that have been nucleated at a given temperature  $T_n$ , *i.e.* reached the super critical size ( $R > R_n^*$ ) during a time interval (0- $t$ ) in the sequential random chain of attachment and detachment of the “structural” units to clusters of the new evolving phase, see e.g. [12]. In the (theoretical) case when the glass is obtained via an infinitely fast quenching of the melt after having performed a complete homogenization of the initial melt, one

could assume that, in the first moments of nucleation heat-treatment at  $T_n$ , in the glass there are no clusters of subcritical size. In such case and if the cluster growth proceeds via the above described scheme, the nucleation process in such ideal system begins with the merging of two “structural” units. For the above initial condition, when the cluster size distribution is zero for all clusters containing more than a few structural units, the following expression describes the time-dependence of the number of super-critical nuclei per unit volume,  $N_V$ , [13]

$$N_V(t) = I_{st} \tau \left( \frac{t}{\tau} - \frac{\pi^2}{6} - 2 \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} \exp\left(-m^2 \frac{t}{\tau}\right) \right), \quad (6)$$

where  $I_{st}$  is the steady-state nucleation rate, and  $\tau$  the nucleation time-lag. Here  $\tau$  characterizes the time of establishment of the steady-state crystal size distribution in a cluster size range including the critical size, and, hence, simultaneously the establishment in this range of cluster sizes of the steady-state value of the nucleation rate.

However, with the cooling rates usually employed for oxide glass preparation (1,000K/min) the initial glass samples already contain – due to cluster formation and growth in the course of the cooling process – a certain amount of crystals,  $N_o$ , having sizes  $R$  larger than the critical size  $R_n^*$  corresponding to the nucleation temperature  $T_n$ . These pre-existing crystals formed during melt cooling compose the *second group* of new phase particles present in the system. Their number density,  $N_o$ , depends on the nucleation and growth rates and cooling conditions. These athermal crystals are capable of deterministic growth at  $T_n$  and, moreover, a part of them having sizes  $R > R_d^*$  can be developed to larger sizes already directly at  $T_d$  without any preliminary heat treatment. The number density of the latter group of clusters is given by a non-zero value of  $N_V^d(t=0)$ . In case of existence of such group of crystallites, the  $N_V^d(t)$ -curve should show a behavior as indicated in Fig.1 by a full line.

An analysis of the experimental data on NaF crystal nucleation indicates that the value of  $N_V^d(t=0)$  is very low (see e.g. Fig.1) and can be neglected. By this reason we will suppose here further on that the *second group* includes only the pre-existing crystals with sizes larger than  $R_n^*$  and smaller than  $R_d^*$ . Being supercritical, these crystals can grow up to the critical size  $R_d^*$

during heat treatment at  $T_n$  and can then be developed at  $T_d$  contributing in such a way to the experimental  $N_v^d(t)$ -curve. The “life time” interval of such contribution depends mainly on the difference between  $R_n^*$  and  $R_d^*$  and the crystal growth rate at  $T_n$ . The influence of the *second* group of crystals on the  $N_v^d(t)$ -curve begins and ends when the largest and smallest crystal from the pre-existing population exceed the value of  $R_d^*$ .

The crystals of the *first group* (crystals nucleated at  $T_n$ ) before their development must move in size space from monomers to  $R_d^*$ , whereas for the pre-existing crystals (*second group*), only from size  $R$  ( $R_n^* < R < R_d^*$ ). Hence the *second group* reaches  $R_d^*$  earlier than the former and, thus, determines the beginning of the  $N_v^d(t)$ -curve. As we already noted above, the effect of pre-existing crystals ceases when the smallest crystals (crystals with size close to  $R_n^*$ ) from this population reach a size  $R_d^*$ . This event results in some peculiarity on the  $N_v^d(t)$ -curve. In other words, beginning at this moment, the  $N_v^d(t)$ -curve is determined only by the nucleation process at  $T_n$ . In our case the inflection in the  $N_v^d(t)$ -curve is attributed with the finishing of the pre-existing crystal population (see e.g. [Fig.1](#)).

It should be noted that the number of crystals of the second group (“athermal” crystals),  $N_o$ , formed during glass preparation, is a poorly controlled quantity. By this reason, in order to eliminate this uncertainty special preliminary heat treatments at given temperatures in period of time enough for establishment of the steady-state crystal size distribution were performed for a  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass [14]. The experimental data obtained in [14] on the nucleation kinetics in the preliminary stabilized glasses were subjected to a theoretical analysis and confirmed by simulation experiment [15, 16, 17]. Hence the “athermal” nuclei affect is the partial case of a general problem of the influence of starting conditions on the transient nucleation kinetics, see e.g. [18, 19].

In order to avoid any such effects in the present study we fitted only the advanced parts of  $N_v^d(t)$ -curves to Eq.(6) to estimate the steady-state nucleation rates,  $I_{st}$ , and the time-lags for nucleation,  $\tau$ , as fitting parameters, since this part is determined solely by the nucleation process at  $T_n$ . The proximity between the critical sizes at  $T_n$  and  $T_d$  makes it possible at a first approximation to neglect the time  $t_o$ .



Fig.5 shows the steady-state nucleation rates and the nucleation time-lags as functions of temperature estimated as fit parameters from the set of experimentally determined  $N_V^d(t)$ -curves into Eq.(6). For a self-consistent description of the experimental data concerning  $I_{st}(T)$ ,  $\tau(T)$ , and  $U(T)$  in the framework of the classical nucleation theory (CNT), we used further the following equations:

$$I_{st}(T) = x \frac{D(T)}{a^4} \sqrt{\frac{\sigma(T)}{k_B T}} \exp(-W^*/k_B T), \quad (7)$$

$$W^* = \frac{16\pi}{3} \frac{a^6 \sigma^3(T)}{\Delta\mu^2(T)}, \quad (8)$$

$$\tau(T) = \frac{2 \cdot 16}{3} \frac{a^4 k_B T \sigma(T)}{\Delta\mu^2(T) D(T)}, \quad (9)$$

$$U(T) = \frac{D(T)}{a} \left( 1 - \exp\left(-\frac{\Delta\mu(T)}{k_B T}\right) \right), \quad (10)$$

where  $D$  is the effective diffusion coefficient determining both the rates of aggregation in nucleation and crystal growth,  $\sigma$  is the specific interfacial free energy of the critical nuclei,  $x$  is the molar fraction of precipitated component (in the present case NaF),  $W^*$  is the thermodynamic barrier for nucleation,  $\Delta\mu$  the difference between the chemical potentials of “structural” units with a size  $a$  in the super-cooled liquid and in the crystalline phase – *i.e.* the thermodynamic driving force for crystallization ( $\Delta\mu = a^3 \Delta G_V$ ),  $k_B$  and  $T$  are the Boltzmann constant and the absolute temperature, respectively.

To employ the above equations one needs to know the value of  $\Delta\mu$  for NaF crystallization. Here  $\Delta\mu$  was determined by the supersaturation relative to the equilibrium concentration  $C^{eq}$  of NaF in the undercooled melt of PTR glass. In our previous work [3],  $C^{eq}$

was estimated as a function of temperature  $T$ . We fitted the experimental data for the equilibrium solubility  $C^{eq}(T)$  by the Schroeder-van Laar equation [20]

$$C^{eq}(T) = C_0 \exp\left(-\frac{\Delta H_m}{RT} \frac{T_m - T}{T_m}\right), \quad (11)$$

where  $T_m$  and  $\Delta H_m$  are melting point and melting enthalpy of dissolved matter (in our case NaF crystals), respectively. In above equation, it is assumed that  $\Delta H_m$  is independent of temperature. In the case of the ideal solutions  $C_0$  is equal 1.

Fig.6 shows the experimental (points) dependence of  $C^{eq}$  on  $T$  taken from ref. [3]. The solid line is plotted by Eq.(11) with  $C_0=10.905$  mol % estimated as fit parameter and  $T_m=1269$  K and  $\Delta H_m = 33.35 \cdot 10^3$  J/mol taken from ref. [21] and ref.[22] respectively. The difference of  $C_0$  from one shows that the solution of NaF in PTR melt is a nonideal solution.

Knowing the concentration  $C$  of the dissolved substance (NaF) and its equilibrium concentration  $C^{eq}$ , the thermodynamic driving force  $\Delta\mu$  for crystallization can be evaluated as

$$\Delta\mu(T) = k_B T \ln\left(\frac{C}{C^{eq}(T)}\right). \quad (12)$$

Diffusivity,  $D$ , specific surface energy,  $\sigma$ , and thermodynamic driving force,  $\Delta\mu$ , determine the crystallization kinetics (see Eqs. (7, 8, 9, 10)). Thus, we varied the temperature dependencies of  $D(T)$  and  $\sigma(T)$  at given values of  $\Delta\mu$  (Eq. (12)) to arrive at the best agreement between calculated and experimental values of  $I_{st}(T)$ ,  $\tau(T)$ , and  $U(T)$ . Hereby the effective diffusion coefficients for nucleation and growth are assumed to be the same. The size parameter  $a$  was considered as a fitting parameter too, estimated as  $4.5 \text{ \AA}$ . It should be noted that this value is very close to the cell parameter of NaF ( $4.6 \text{ \AA}$ ). The fitting procedure deals simultaneously with the set of all experimental data, but is facilitated by the fact that the influence of  $\Delta\mu$  is stronger on  $I_{st}$  than on  $\tau$  and  $U$ , whereas  $D$  affects more  $\tau$  and  $U$ .

The following fitting equations were used for  $\sigma$  (J/m<sup>2</sup>) and  $D$  (m<sup>2</sup>/s):

$$\sigma(T) = \sigma_0 [1 - \alpha(T - T_{\max})], \quad (13)$$

$$D(T) = D_1(T) \cdot f_k \left( \frac{T_k - T}{\delta T} \right) + D_2(T) \cdot f_k \left( \frac{T - T_k}{\delta T} \right), \quad T_k = 773 \text{ K}, \quad (14)$$

where

$$\sigma_0 = 0.0735 \text{ J/m}^2, \quad T_{\max} = 758.4 \text{ K}, \quad \alpha = 1.0162 \cdot 10^{-3} \text{ K}^{-1},$$

$$D_1(T) = 1.116 \cdot 10^{14} \exp \left( -\frac{51 \cdot 10^4}{RT} \right), \quad D_2(T) = 2.468 \cdot 10^{-2} \exp \left( -\frac{29 \cdot 10^4}{RT} \right),$$

$$f_k(x) = \frac{1}{2} [1 + \tanh(x)].$$

The above equations need a few comments.  $T_{\max}=758.4 \text{ K}$  in Eq. (13) is the temperature of maximum nucleation rate (see Fig.5a). In such way we fixed the value of  $\sigma(T_{\max}) = \sigma_0$  that together with the other parameters yields the correct maximum value of the steady-state nucleation rate. The temperature dependence of the interfacial free energy is shown in Fig.7. To describe the temperature dependence of the nucleation time-lags and also to achieve the correct value of  $U(T)$ , a combination of two diffusion coefficients corresponding to low ( $D_1$ ) and high ( $D_2$ ) temperatures was employed (see Fig. 8). The transition from  $D_1$  to  $D_2$  was performed via a function  $f_k$ .  $\delta T$  and  $T_k$  are the width of this transition and its average temperature, respectively.

## 5. Discussion

Since the PTR glass contains only 5 mol% NaF, the formation of NaF crystals results in a strong depletion in F of the residual melt, and when the NaF content in the melt reaches equilibrium, the very early stage of coarsening begins [12]. However, in our case, we did not achieve a detectable coarsening stage due to insufficient experimental time. The evolution of the residual melt composition and related phenomena were investigated in detail in some of our previous papers [2, 3, 4, 5]. The saturation of the crystal size *versus* time plot (Fig.3) reflects the attainment of an equilibrium between the NaF crystals and the residual melt. As we noted early, to obtain the temperature dependence of the crystal growth rates we used only the initial part of the  $R(t)$  time plots, such as that shown in Fig.3, since in the early stages of the phase

transformation crystal growth is determined by a time-independent effective diffusion coefficient. The change of the residual melt composition can be also neglected for the analysis of the nucleation kinetics due to the extremely small nuclei sizes and hence very small volume fraction of crystalline phase.

The fitting procedure described in Section 4 is complex because it simultaneously includes all parameters governing the overall crystallization kinetics (the steady-state nucleation rates, the time-lags for nucleation, and the crystal growth rates) measured in a wide temperature interval covering about three hundred degrees - from 470 °C to 750 °C. The fitting parameters (the surface free energy and the effective diffusion coefficient) shown in Figs.7 and 8 as a function of temperature, respectively, together with the thermodynamic driving force give a very reasonable description of the experimental data (please compare the experimental points and calculated lines in Figs.4 and 5). The self-consistent description of both nucleation and growth kinetics using the same temperature dependencies of  $\sigma(T)$  and  $D(T)$  gives indirect evidence for its validity. Therefore the following comments on the above dependencies can be made.

The specific surface energy,  $\sigma$ , estimated via the experimental nucleation rates in the framework of CNT for silicate glasses and metallic glasses, as a rule, increases with temperature (see e.g. [23]). It should be stressed that, as opposed to PTR glass, in these cases the crystal composition is equal or close to that of its liquid. For PTR glass, however,  $\sigma$  weakly *decreases* with increasing temperature (Fig.7). Finally, together with a decreasing thermodynamic driving force this results in an increase of the thermodynamic barrier shown in Fig.9.

The value of  $\sigma$  estimated via nucleation rates relates to the nuclei with critical or near critical size. Thus, the evolution of  $\sigma$  shown in Fig.7 is the combination of the pure temperature dependence and the size dependence resulting from the increase of critical size with temperature shown in Fig.9. This size dependence can be, in principle, incorporated into Eqs.(7,8,9), e.g. as was done in ref.[21]. However, despite its long history, the problem of a size dependent specific interfacial free energy remains open [24, 25, 26, 27].

The temperature dependence of the effective diffusion coefficient that governs both nucleation and growth kinetics is shown in Fig.8. Its activation enthalpy decreases with temperature. Such behavior is common for temperature activated processes. It should be noted that the experimental data for the nucleation time-lag relates to the temperatures interval that includes both  $D_1$  (low temperatures) and  $D_2$  (high temperatures), whereas the  $U$  measurements

were performed only at temperatures corresponding to  $D_2$ . Therefore, to complete the analysis of the effective diffusivity (Fig.8), we estimated the diffusion coefficient in an independent way by the Stokes-Einstein-Eyring equation

$$D_\eta = k_B T / a\eta, \quad (15)$$

using viscosity data available for PTR glass [28] that are described by the following Vogel-Fulcher-Tammann equation:

$$\log \eta = -2.40 + 4740 / (T - 416), \quad (16)$$

where the viscosity and temperature are given in Pa·s and K, respectively.

The difference between  $D$  and  $D_\eta$  does not exceed 1.5 orders of magnitude and this is an unexpected result. The effective diffusion coefficient  $D$  estimated from NaF crystallization kinetics reflects the transport of the “building” elements involved in the formation of NaF crystals. Since the PTR glass already contains 15%Na<sub>2</sub>O, the kinetics of NaF crystallization is limited by the fluorine mobility. Despite the deficiency of diffusion coefficient data for fluorine in silicate glasses, we expect, based on F-O interdiffusion coefficient measurements for some melts of the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system [29], that  $D_F$  is 5-8 orders of magnitude *higher* than  $D$  evaluated from NaF crystallization kinetics. Here it should be recalled that the diffusion coefficient of sodium in common sodium calcium silicate glasses varies between 10<sup>-13</sup> and 10<sup>-10</sup> m<sup>2</sup>/s (see e.g. [30, 31]) in the temperature interval 700-800 K (the temperatures of interest here), then these values are also considerably higher than  $D$ . Thus one could suppose that the transport processes of F and Na determining crystallization kinetics are complex and may be somewhat correlated with viscous flow. For instance, “structural units” of the glass-forming melt could perhaps cooperatively move to liberate space for the NaF crystal boundary advance. Here it should be recalled that the reduction of the NaF content in PTR glass results in the strong increase of viscosity [3]. However the correlation between  $D$  and  $D_\eta$  decreases with decreasing temperature, as one can see from Fig.10 (the ratio  $D/D_\eta$  versus temperature). This effect is known as decoupling (or breakdown) and according to Ediger *et al.* [32] it is expected in fragile

glasses in the neighborhood of the glass transition temperature  $T_g$ . Please recall that according to ref. [28] the fragility index  $m$  for PTR glass is about 33. This means that PTR glass is positioned between the typical “strong” and “fragile” glasses.

## 6. Conclusions

The detailed kinetics of NaF crystallization in UV-unexposed PTR glass was experimentally studied for the first time. Steady-state nucleation rates, nucleation time-lags and crystal growth rates were estimated in a temperature interval covering almost three hundred degrees, from  $T_g \sim 470^\circ\text{C}$  up to  $750^\circ\text{C}$ . A self-consistent description of these data in the framework of CNT was presented using the interfacial free energy and the effective diffusion coefficient as adjustable parameters. The diffusivities calculated from crystallization kinetics and viscous flow undergo a decoupling phenomenon already demonstrated for other fragile glasses.

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### Figure captions

Fig.1 Number density of NaF crystals developed at  $T_d=650^\circ\text{C}$  versus time of nucleation treatment at  $T_n=530^\circ\text{C}$ . The lines are plotted by Eq.(6).

Fig.2 Transmitted light optical micrographs of PTR glass samples treated at  $690^\circ\text{C}$  for 25 min.

Fig.3 Radius of NaF dendrite versus treatment time at  $T=650^\circ\text{C}$ .

Fig.4 Growth rates of NaF crystals versus temperature. The solid line is plotted by Eq.(10).

Fig.5 Steady-state nucleation rates of NaF crystals (a) and corresponding time-lags (b) versus temperature. The solid lines result from calculations by a) - Eq.(7) and b) - Eq.(9).

Fig.6 Equilibrium content of NaF (mol%) in PTR glass as a function of temperature. The solid line is plotted by Eq.(11) with proper parameters.

Fig.7 Specific free energy of the interface critical nucleus / liquid versus temperature. The line is plotted by Eq.(13).

Fig.8 Effective diffusion coefficient,  $D$ , estimated from crystallization kinetics and  $D_\eta$  estimated from viscosity data via the Stokes-Einstein-Eyring equation.

Fig.9 Thermodynamic barrier for nucleation,  $W^*$ , and critical size,  $R^*$ , versus temperature.



Fig.10 The ratio of  $D$  to  $D_\eta$  versus temperature.