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Crystallization in fluoride glasses[1]

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Abstract

Fluoride glasses which are used for passive and active optical fibers are subject to devitrification, especially during fiber-drawing. Kinetic parameters may be obtained through isothermal and nonisothermal methods. Basic relations deriving from the Mehl–Avrami–Johnson approach allow the determination of activation energy E_a and Avrami exponent n. The paradox of activation energy is expressed in terms of correlation between E_a value and binding energy, which raises the question of the physical meaning of activation energy. Various stability factors are listed and their validity discussed. The important problem of nucleation in fluoride glasses emphasizes the role of anionic oxygen in the nucleation mechanism. The crystallization behavior of the main fluoride glasses, including cadmium fluorochloride glasses, is reported in relation to fiber-drawing ability.

Keywords: Activation energy; Crystallization; Fluoride; Glass; Nucleation; Stability

1. Introduction

The specific properties of heavy metal fluoride glasses (HMFG) make them suitable for various optical applications based on their extended transmission range in the IR spectrum. Optical fibers are required, in most cases, either for passive use such as sensing, laser power delivery and thermometry, or for lasing and optical amplification. At the early stage of development, the potential of these glasses for ultra-low-loss fibers was emphasized [1], but it turned out that optical losses could not be decreased enough to approach the intrinsic transmission limits.

While fluoride glasses also exhibit potential UV transmission and low dispersion, no bulk optical components could be developed and tested, mainly because optical quality remained too limited. The intrinsic instability of HMFG with respect to devitrification

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[1] Dedicated to Professor Hiroshi Suga.

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is considered as the major problem in their technological development, especially for low-loss optical fibers. Consequently, it is of practical importance to assess the parameters ruling crystallization and to separate intrinsic features and extrinsic factors.

In addition, some fundamental questions still await satisfactory answers. For example, what is the correlation between glass stability and the viscosity/temperature profile? What are the structural changes in "fragile" glasses as defined by Angell [2]? Is there a physical meaning for activation energy at viscous flow? Why do more stable glasses exhibit low activation energy?

This paper intends to provide an overview of crystallization behavior in fluoride glasses and to provide information for discussion.

2. Basic relations

Devitrification may be quantified in several ways. The basic approach focuses on the crystalline fraction x in a bulk glass sample. When x is very small, typically 10^{-5}–10^{-6}, samples do not exhibit much scattering losses and are considered as completely vitreous. However, the measurement of x, or the temperature at which x reaches a given value, gives access to the calculation of the kinetic parameters for devitrification.

Most practical relations are based on the Mehl–Avrami–Johnson approach [3,4] leading to the expression

$$x = 1 - \exp(-kt)^n \tag{1}$$

where t is time and k is a constant which encompasses nucleation and crystal growth rates. The value of the Avrami exponent n is correlated with nucleation and crystal growth mechanisms [5–7]. Relation (1) is valid in isothermal conditions and the evolution of k versus temperature is assumed to be Arrhenian

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

with E_a the activation energy, T temperature, and R the rare gas constant.

When x is small [8], a first-order development of relation (1) leads to

$$x = \pi/3 I U^3 t^4 \tag{3}$$

Time–temperature–transformation curves may be calculated [6] from this expression. Different thermal zones may be defined according to the stability of the glass versus devitrification. Such a curve, as illustrated in Fig. 1, reports for each temperature the time needed for achieving a given transformation rate x, e.g. 10^{-4}. When time reaches a very high value, the glass may be considered as stable. This happens at high and low temperatures, T_{max} and T_{min} respectively. These two temperatures, together with the liquidus temperature T_l and glass transition temperature T_g define the different stability domains of the glass (Table 1). The isothermal analysis is generally based on relation (1) with a simple transformation

$$\ln(-\ln(1 - x)) = n \ln k + n \ln t \tag{4}$$

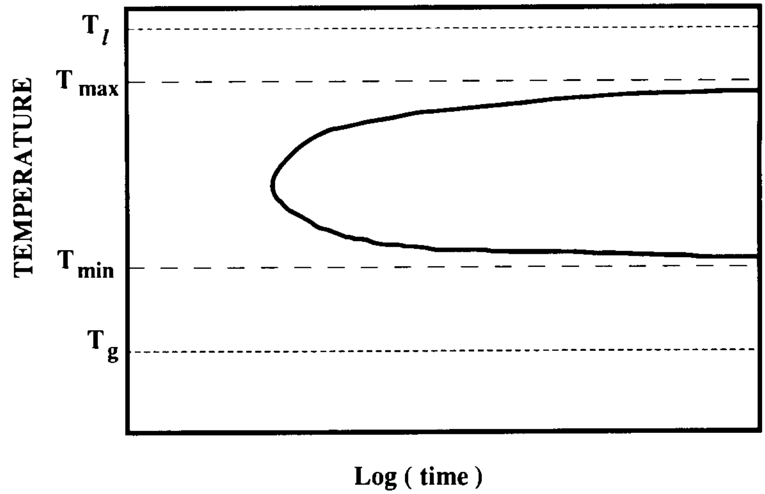

Fig. 1. Typical time–temperature–transformation curve defining different stability ranges according to liquidus, glass transition and limiting temperatures.

Table 1
Stability regions as a function of temperature

	T_g		T_{min}		T_{max}		T_l	
Stable glass		Metastable liquid		Unstable liquid		Metastable liquid		Stable liquid

In this way, k and n may be calculated, and the activation energy is easily obtained from a set of values of k for different temperatures.

For practical reasons, isothermal measurements are not always possible. Nonisothermal methods have been investigated, and their conditions of validity have been studied by various authors [5,9–12]. Activation energy is calculated using the general relation

$$\ln\left(\frac{T^{m}}{\alpha}\right) = \frac{E_a}{RT} + \text{constant} \tag{5}$$

with α the heating rate, T the temperature of the exotherm maximum, and E_a the activation energy.

The exponent m is an integer equal to: 0, according to Chen [12]; 1, according to Kissinger [13]; and 2, according to Osawa [11]. The plot of the function $\ln(T^{m}/\alpha)$ versus $1/T$ gives a straight line with a slope equal to E_a/R. While it may sound strange that three different relations could describe the same phenomenon, a comparative study by Moore [14] showed that they lead to similar values of E_a. The value of n may also be calculated using nonisothermal data either from Osawa's relation [11] or from Piloyan's approach [15].

Among practical advantages of nonisothermal methods, one may quote:

(i) More accessible equipment: DTA is sufficient for obtaining a reliable value for activation energy;
(ii) They apply to crystallization phenomena that are more rapid than in isothermal stages;
(iii) Consequently, they provide information at temperatures too high for isothermal methods.

While the above relations are widely used for devitrification studies, their field of application should be discussed. The Mehl–Avrami–Johnson approach [3,4] is not the only one, and other relations based on different assumptions could also apply (see, for example, Ref. [16]). Also, it is implicitly assumed that only a single crystalline phase is growing from the melt. Moreover, this phase should have the same composition as the melt. In multicomponent glasses, these conditions are frequently not satisfied.

3. The paradox of activation energy

Activation energy may be the most accessible kinetic parameter: a set of DTA or DSC scans is usually sufficient to calculate it with a reasonable accuracy. While its value may depend on the method, significant comparisons may be achieved using the same formula [5].

It is generally admitted that activation energy provides two information elements: firstly, its value is assumed to be the same as that of viscous flow in the same thermal range; and secondly, a low value of E_a is correlated with a high stability against devitrification. This observation raises a first question about the physical meaning of activation energy. Classically, one would expect this energy to be a gap separating the metastable state of undercooled liquid and the stable state of the crystalline phase. Then, a high E_a should correspond to difficult crystallization, not to the reverse situation.

Considering more generally the evolution of viscosity versus temperature (Fig. 2), the plot of log η versus $1/T$ which is linear in the ideal case of Arrhenian behavior, e.g. vitreous silica, exhibits limited or strong deviations from linearity for most glasses, especially fragile glasses as defined by Angell [2]. The tangent to the curve is assumed to be equal to E_a/R, which makes calculation of the activation energy possible at any melt temperature.

Glass transition corresponds to the transition between the solid and liquid state. This implies the breaking of chemical bonds. Obviously, weaker bonds will break first. When temperature increases, stronger bonds are broken until quasi-molecular units prefiguring gaseous species are formed. However, one would expect activation energy to be correlated with the energy required for breaking chemical bonds. Therefore, it is paradoxical that activation energy is very high at T_g when thermal motion affects the weaker bonds of the modifiers, and much lower at high temperature when the stronger bonds of the network are disrupted.

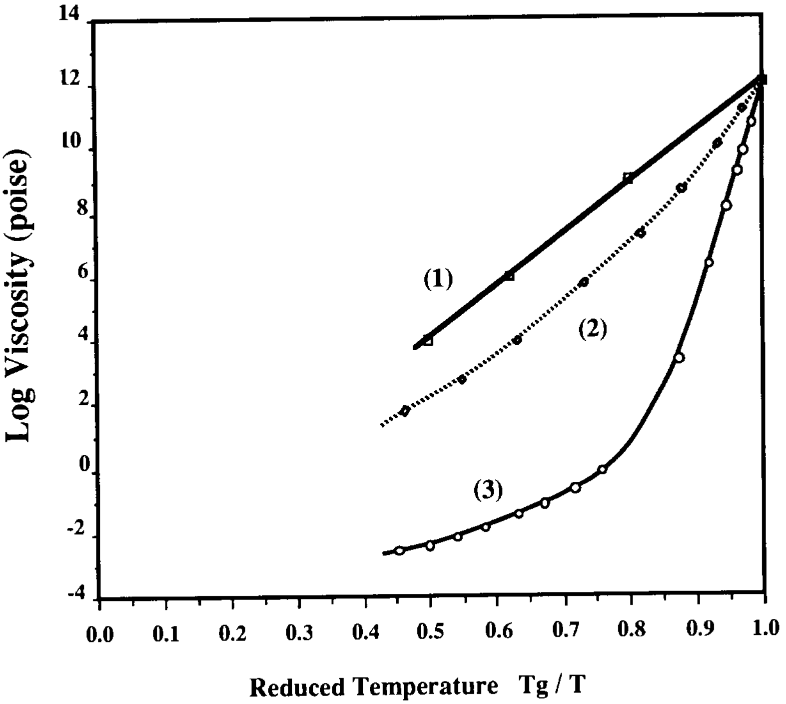

Fig. 2. Evolution of viscosity in logarithmic scale versus reduced reciprocal temperature for silica (1), soda lime glass (2) and fluorozirconate glass (3). They correspond to Arrhenian, Fulcher-type and fragile behaviors, respectively.

While it is not the purpose of this paper to bring an answer to this apparent paradox, the importance of the underlying question of the physical meaning of the activation energy must be outlined. It should be a major element in the understanding of the intrinsic instability of most fragile glasses versus devitrification.

4. Qualitative approach of glass stability in fluoride glasses

The resistance of ionic glasses against devitrification is obviously correlated with composition. It is often difficult to quantify this correlation. The ultimate test simply consists in manufacturing an optical component, either bulk sample or optical fiber, and measuring scattering losses induced by crystallization. This method is time-consuming and costly. Another possibility consists of making samples of increasing thickness: the maximum thickness may define a stability scale. However, this requires rather large melts, larger than current batch size at laboratory scale.

For this reason, researchers have tried to assess glass stability via DTA or DSC measurements on small samples.

Several criteria have been defined in this way [6]. The different temperatures used in the various formulae are: T_g, glass transition; T_x, onset of crystallization; T_c, maximum of exotherm; and T_m, melting temperature. Current stability factors are

$$\Delta T = T_x - T_g \tag{8}$$

The Hruby factor [17]

$$\mathrm{Hr} = \frac{T_c - T_g}{T_m - T_c} \tag{9}$$

$$H' = \frac{T_x - T_g}{T_g} \tag{10}$$

From Ref. [18]

$$S = \frac{T_x - T_g}{T_g}(T_x - T_c) \tag{11}$$

Stability may also be quantified simply from the value of the critical cooling rate CCR, defined as the cooling rate for which the crystalline fraction x is small enough to be neglected. It may be calculated from the TTT curve, or from a relation introduced by Barandiaran and Colmeneiro [19]

$$\ln R = A - \frac{B}{\Delta T_c^2} \tag{12}$$

where R is the cooling rate, A and B are constants, and ΔT_c is the separation between melting temperature and crystallization temperature on cooling. A linear plot is obtained from experimental data, and $A = \ln(\mathrm{CCR})$.

Finally, activation energy may also indicate the stability factor insofar as correlation between low E_a and stability is assumed.

All these factors exhibit advantages and limitations. The critical cooling rate seems suitable for the casting of optical bulk components which do not undergo further heating beyond T_g. However, stability factors encompass both cooling and reheating stages, which is closer to the thermal history of optical fibers drawn from preforms. All factors have been successfully applied for studying stability evolution in a glass family when composition is linearly modified. They provide an easy way of identifying the optimum composition.

There may be some practical problems. Measuring CCR requires a set of DTA scans on cooling, which takes several days. The TTT curves also require numerous DSC scans and are not easily obtained for small values of the crystalline fraction. The other stability factors are calculated from a single DTA or DSC scan. However, they may be ambiguous or less significant when there are several crystallization or melting peaks. The factors Hr and S are more sensitive to this than ΔT and H'.

A more fundamental limitation of these numerical factors lies in their practical determination. Since they are implemented on small samples, typically 10–50 mg in weight, they encompass surface crystallization. In addition, extrinsic nucleation may be important or even predominant in some cases, particularly for compositions which are very sensitive to moisture contamination, as water concentration usually exceeds tens of ppm in the measuring cells. The limited significance of DSC scans is illustrated by the fiber drawing of the ZBLA glass which is achieved at around 400°C [20] while its DSC crystallization peak has its maximum at 406°C [18]. Also, this raises the questions of heterogeneous nucleation and processing influence.

5. Nucleation in fluoride glasses

It is largely assumed that the intrinsic instability of fluoride glasses accounts for scattering losses in fluoride glass optical fibers [21]. However, some extrinsic factors have been identified. Mitachi and Tick carried out a systematic study of the effect of oxygen concentration on the cooling rate of various fluoride glasses [22]. Also, correlation between oxygen content and scattering optical losses was reported by NTT researchers [23]. This indicates that anionic oxygen plays a significant part in the nucleation process. The origin of residual oxygen in fluoride glasses is linked to starting materials, fluorinating conditions and hydrolysis from the working atmosphere. The mechanism of nucleation involving oxygen is largely unknown although it has been accurately described elsewhere [24]. Under specific conditions, an oxygen-rich vitreous phase may separate from fluoride glass. When it is formed at the glass surface, it accounts for the defects observed on the neck cone of preforms [21,25] or for the so-called "rubber state" of fluoride glasses [25]. When this phase is located in the bulk glass, it makes a source of optical scattering.

This heterogeneous phase which contains oxygen is a source of nuclei for fluoride glass crystallization. The accurate observation of the surface of a fluoride glass sample shows that the formation of this heterogeneous phase precedes surface crystallization. While this phase separation obviously depends on the concentration in anionic oxygen within the fluoride melt, it is also ruled by the classical nucleation and growth mechanism. The observed influence of processing conditions upon scattering may be largely explained in this way.

6. Kinetic parameters in fluoride glasses

More devitrification studies have focused on fluorozirconate glasses because optical fibers need to be optimized. While few TTT curves are reported [26–28], various studies have been implemented using isothermal and nonisothermal methods. The Avrami exponent n was found to be close to 3 in most cases [26,29]. This was interpreted on the basis of three-dimensional growth from a constant number of nuclei. It appears consistent with the observed fiber-drawing ability of ZBLA- and ZBLAN-based glasses. Activation energy ranges from 40 to 90 kcal mol^{-1}, depending on vitreous systems and possibly on processing. ZBLAN glass exhibits lower E_a values than ZBLA or ZBL.

Incorporation of chlorine in fluoride glasses modifies kinetic parameters [30]. While the activation energy is 30 kcal mol^{-1} in the 50 ZrF_4–$30BaF_2$–$5ThF_4$–$3LaF_3$–12 RbCl glass, the value of the Avrami exponent was found to vary according to temperature range. This unexpected result corresponds to a change in crystallization mechanism, as two crystallization peaks were observed at high heating rate.

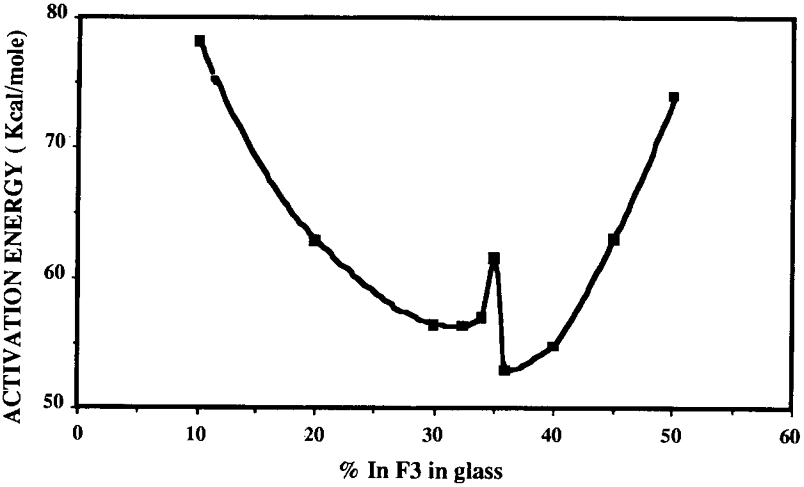

Fig. 3. Evolution of activation energy for crystallization as a function of InF_3 concentration in the $x InF_3$-(60-x)ZnF_2-20BaF_2-20SrF_2 glass.

Indium fluoride glasses have been studied more recently because they have lower phonon energy than fluorozirconate glasses [31], resulting in extended possibilities for both active and passive fibers [31]. In these glasses, the values of n and E_a depend strongly on composition range [28]. A peculiarity was observed in the InF_3–ZnF_2–BaF_2–SrF_2 glass: an increase in activation energy at 35% InF_3, as shown in Fig. 3. The Avrami exponent was found to be close to 3 for the mostly stable glass compositions, while it reaches higher values in ternary or quaternary glasses such as IZBS.

Cadmium fluorochloride glasses are attractive materials for optical amplification at 1.3 μm. Unfortunately, fiber drawing attempts have been largely unsuccessful as preforms crystallize on reheating. This was surprising, as DSC scans of cadmium halide glasses suggest they should be even more stable than ZBLAN glass. While activation energy is found to be 35 kcal mol^{-1} at 630 K and 56 at 590 K, the n values are in the range 2–4, which suggests that these glasses are rather stable on crystallization. In practice, they crystallize more rapidly than fluorozirconate or fluoroindate glasses. While these latter glasses keep a constant number of nuclei in the drawing temperature range, it seems that intense nucleation occurs in cadmium halide glasses. This is largely unexpected and unexplained if we consider thermal analysis data. There could be a size effect influencing crystallization behavior.

7. Conclusion

Devitrification studies of fluoride glasses have been stimulated by the observed crystallization phenomena in bulk samples and in optical fibers. For current composition research, several stability factors could be used for assessing the optimum glass compositions.

Various studies have been implemented on fluorozirconate, fluoroindate, fluorogallate and cadmium fluorochloride glasses. The values for activation energy and Avrami exponent *n* were calculated. It appears that only glasses with an *n* value not larger than 3 could be drawn into a fiber using the preform method. Problems with cadmium halide glasses could relate to excessive nucleation at the drawing temperature.

Devitrification studies of fluoride glasses raise fundamental questions, in particular: the role of anionic oxygen in the nucleation of fluoride glasses; the paradox of activation energy; and the physical meaning of activation energy and its correlation with glass stability.

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