

EVALUATION OF THE STABILITY OF SUBSTITUTED InF_3 GLASSES BY DIFFERENTIAL THERMAL ANALYSIS

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(Received January 10, 1996; in revised from October 3, 1996)

Abstract

The thermal properties and devitrification behaviour of substituted InF_3 glasses were studied by means of differential thermal analysis. A comparison of various simple quantitative methods to assess the level of stability of multicomponent fluoride glass systems was also made. Most of these methods are based on critical temperatures. In this paper, a new parameter, $k_d(T)$, is introduced to the stability criteria. The stabilities of several substituted InF_3 glasses were evaluated experimentally and correlated with the activation energies of crystallization via this new kinetic criterion and compared with those evaluated by other criteria.

Keywords: DTA, stability, substituted InF_3 glasses

Introduction

Multicomponent vitreous fluorides [1–8] are potential optical materials and multispectral optical components [9] by virtue of their high transparency from the near-ultraviolet ($\approx 0.3 \mu\text{m}$) to the mid-infrared ($\approx 0.6 \mu\text{m}$). However, only a few of them have been used in practice. One of the problems concerning the development of these multicomponent fluoride glasses is their glass stability and chemical durability. No simple way exists at present to formulate the correlation between the ideal composition and the stability of these glasses. According to Iqbal [10], the concept of glass stability refers to how slowly the glass melt could be cooled and how slowly the glass sample could be reheated without crystallization.

In order to evaluate the level of stability of multicomponent fluoride glass systems, different simple quantitative methods have been suggested. Most of these methods [11–15] are based on critical temperatures such as the glass transition temperature, the crystallization temperature or the melting temperature. Some of them [16, 17] are based on the glass crystallization constant k . Others [18–20] are based on the crystallization activation energy. These thermal pa-

rameters are easily and precisely obtained by means of DTA or DSC during the heating processes of glass samples. Dietzel [11] introduced the first glass criterion, thermal stability $\Delta T = T_x - T_g$. By using the critical temperatures, Hruby [14] developed the Hr criterion, $Hr = (T_x - T_g) / (T_l - T_x)$. On the basis of the Hr criterion, Saad and Poulain [15] obtained other two criteria, the weighted thermal stability H' and S criteria, $H' = (T_x - T_g) / T_g$ and $S = (T_p - T_x)(T_x - T_g) / T_g$. In the present work, a new kinetic parameter is introduced to the glass stability criteria.

Experiment

Glass preparation

The starting materials were NaF, BaF_2 , CaF_2 , CdF_2 , MgF_2 , SrF_2 , ZnF_2 , InF_3 , YF_3 and GeF_4 . A batch of 20 g was mixed with excess ammonium bifluoride (NH_4FHF) as a precaution to convert trace oxide impurities to fluoride. Glasses were melted for 4–5 h in a vitreous carbon crucible with a resistance furnace. After complete melting, the glass melts were cast by pouring into open brass moulds. Glass samples were annealed near the glass transition temperature. The substituted InF_3 glasses had the following mole composition formulae: $36\text{InF}_3 - 20\text{BaF}_2 - 20\text{SrF}_2 - 20\text{ZnF}_2 - 4\text{RF}$ (IBSZR), where RF is NaF, CaF_2 , CdF_2 , MgF_2 , YF_3 or GeF_4 .

Differential thermal analysis

DTA measurements were carried out with a Netzsch thermal analyser (model 409E/3) with an accuracy of better than $\pm 1^\circ\text{C}$. For non-isothermal experiments, glass samples were heated from 20 to 700°C at heating rates varying from 2 to

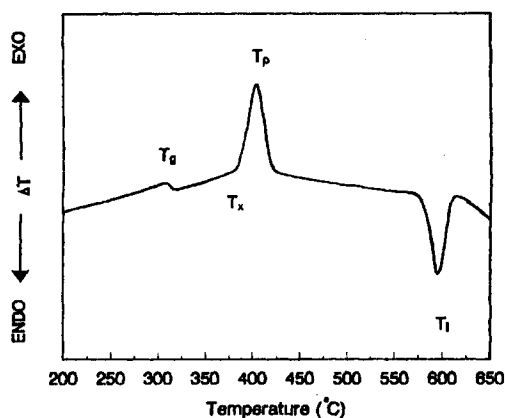


Fig. 1 Typical DTA curve of the substituted InF_3 glass at heating rate $10^\circ\text{C min}^{-1}$

20°C min⁻¹. Bulk glass pieces (10–20 mg) instead of powder were used to avoid problems with particle size distribution. In this case, Al₂O₃ powder was added to improve heat transfer and was also used as reference material. A typical result is given in Fig. 1.

Theoretical analysis

The relationship between the crystallization fraction and the nucleation and growth rate is given by the John-Mehl-Avrami equation:

$$x = 1 - \exp[-(kt)^n] \quad (1)$$

where x is the volume fraction crystallized after time t , n is the Avrami exponent, and k is the reaction rate constant, encompassing nucleation and crystal growth factors, whose temperature dependence is generally expressed by the Arrhenian-type equation

$$k = \nu \exp(-E/RT) \quad (2)$$

where ν is the frequency factor, E is the apparent activation energy, R is the ideal gas constant and T is the isothermal temperature in degrees Kelvin.

In a non-isothermal DTA experiment, the temperature is changed linearly with time at a known scan rate $\alpha (=dT/dt)$:

$$T = T_0 + \alpha t \quad (3)$$

where T_0 is the starting temperature, and T is the temperature after time t . As the temperature constantly changes with time t , k is no longer a constant, but varies with time in a more complicated form, and Eq. (1) becomes:

$$x = 1 - \exp[-(k(T - T_0)/\alpha)^n] \quad (4)$$

or

$$x = 1 - \exp \left[- \left(\int_0^t k(t) dt \right)^n \right] \quad (5)$$

If the rate of transformation is maximum at the DTA curve peak, then ($T=T_p$):

$$d^2x/dt^2 = 0 \quad (6)$$

After deducing and rearranging Eq. (5), Kissinger [21] developed a method for a non-isothermal analysis of devitrification. The final relation was as follows:

$$\ln(T_p^2/\alpha) = \ln(E/R) - \ln v + E/RT_p \quad (7)$$

Therefore, a plot of the logarithm of the peak temperature squared divided by the heating rate α was proportional to the reciprocal of T_p , with slope E/R and intercept $\ln(E/R) - \ln v$. In this way, one can obtain E , V and $k(T)$. Surinach [16] proposed the $k(T_g)$ criterion, and Hu [17] developed the $k(T_p)$ criterion:

$$k(T_g) = v \exp(-E/RT_g) \quad (8)$$

$$k(T_p) = v \exp(-E/RT_p) \quad (9)$$

Thus, the values of these two parameters indicate the tendency to glass devitrification on heating. The higher their values, the greater the tendency to devitrification. The formation of glass is a kinetic process. It is reasonable to assess the glass stability via the kinetic parameter $k(T)$. Here, a stable factor ($B = \Delta T/T_i$) is introduced and a new criterion is defined as $k_d(T)$:

$$k_d(T) = v \exp(-BE/RT) \quad (10)$$

where T is the temperature between T_g and T_p . Just like the $k(T)$ criteria, the lower the value of $k_d(T)$, the higher the thermal stability of the glass should be. The obvious advantage of this method is that it can evaluate the glass stability in a broad temperature range, rather than at one temperature such as T_g or T_p .

Results

The characteristic temperatures from the DTA curves are given in Table 1. The thermal stabilities of these substituted InF_3 glass samples can be estimated by using these critical temperatures, T_g , T_x , T_p and T_i . The existing stability criterion parameters (ΔT and Hr) based on these critical temperatures are also listed in Table 1.

It is known that these criteria of glass stability allow a prediction of the tendency to devitrification. It is suggested that the higher values, the higher should be the glass thermal stability. According to this suggestion, the parameters, ΔT and Hr in Table 1 show that the glass sample IZBSMg is more stable than the other five glass samples. The glass stability sequence at different heating rates is almost always IZBSMg > IZBSCd > IZBSY > IZBSGe > IZBSCa > IZBSNa. However, the devitrification is a kinetic process, and this stability sequence does not fit with the actual melting processes of the substituted InF_3 glasses. Thus, it is reasonable to assess the glass stability *via* the kinetic parameters.

To obtain the kinetic parameters of crystallization, Eq. (7) is applied. Figure 2 presents the evolution of $\ln T_p^2/\alpha$ vs. $1/T_p$. The plots were found to be straight lines

Table 1 Physical properties of substituted InF_3 glasses

$\alpha = 5^\circ\text{C min}^{-1}$							
Sample	$T_g/^\circ\text{C}$	$T_x/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_i/^\circ\text{C}$	$\Delta T/^\circ\text{C}$	Hr	E/R
IZBSNa	303	361	372	548	58	0.310	$2.425 \cdot 10^4$
IZBSCa	301	372	381	590	71	0.327	$3.123 \cdot 10^4$
IZBSCd	298	380	390	589	82	0.392	$2.326 \cdot 10^4$
IZBSMg	306	396	404	607	90	0.427	$1.806 \cdot 10^4$
IZBSY	303	384	395	598	81	0.379	$2.320 \cdot 10^4$
IZBSGe	299	377	387	601	78	0.348	$2.385 \cdot 10^4$
$\alpha = 10^\circ\text{C min}^{-1}$							
Sample	$T_g/^\circ\text{C}$	$T_x/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_i/^\circ\text{C}$	$\Delta T/^\circ\text{C}$	Hr	ν/sec^{-1}
IZBSNa	307	370	383	551	63	0.348	$6.447 \cdot 10^{15}$
IZBSCa	302	375	388	598	73	0.327	$2.090 \cdot 10^{20}$
IZBSCd	301	390	405	595	89	0.434	$4.210 \cdot 10^{14}$
IZBSMg	311	405	420	610	94	0.459	$7.306 \cdot 10^{10}$
IZBSY	309	395	406	602	86	0.415	$3.193 \cdot 10^{14}$
IZBSGe	303	388	400	603	85	0.395	$1.282 \cdot 10^{15}$

in accordance with Eq. (7). The slope E/R , and frequency factor ν are then evaluated by a least-squares fitting method. Table 1 lists the values utilized in these calculations. When the values of E/R and ν are known, the kinetic parameters can be calculated. The kinetic parameters $k(T)$ and $k_d(T)$ of the substituted InF_3 glasses are listed in Table 2.

Hu and Surinach suggested that the lower the value of $k(T_g)$ or $k(T_p)$, the higher should be the thermal stability of the glass. Accordingly, the data on $k(T_p)$ in Table 2 indicate that the glass sample IZBSMg is the most stable of these glass samples at different heating rates. However, it is difficult to obtain the same stability sequence for the substituted InF_3 glasses by this criterion.

Surinach's [16] criterion $k(T_g)$ is contrary to Hu's [17] criterion $k(T_p)$ and to the actual melting process of this fluoride glass system. The result shows that this criterion does not fit the fluoride glass system.

The data on $k_d(T_g)$, $k_d(T_x)$ and $k_d(T_p)$ in Table 2 also show that the glass sample IZBSMg is the most stable, and the stability sequence is IZBSMg > IZBSY > IZBSCd > IZBSGe > IZBSNa > IZBACa at various heating rates. This stability result agrees with the actual melting processes of the substituted InF_3 glasses.

Discussion

According to Mackenzie [22] and Poulain [23], MgF_2 and YF_3 are good structural intermediates. They are able to participate in the continuous glass network and can increase the glass stability and chemical durability. However, CaF_2 , CdF_2 and NaF are glass modifiers. According to Cottrant [24], glass modifiers have two contradictory effects on glass formation in multicomponent systems: 1) some of them tend to induce crystallization, while 2) some of them enhance the covalence of the glass former, increasing the polymerization of the species in the liquid phase and favouring glass formation. As shown above, CaF_2 and NaF have a higher tendency to crystallization, while CdF_2 has a higher glass stability. The result of the $k_d(T)$ criterion agrees with these assumptions.

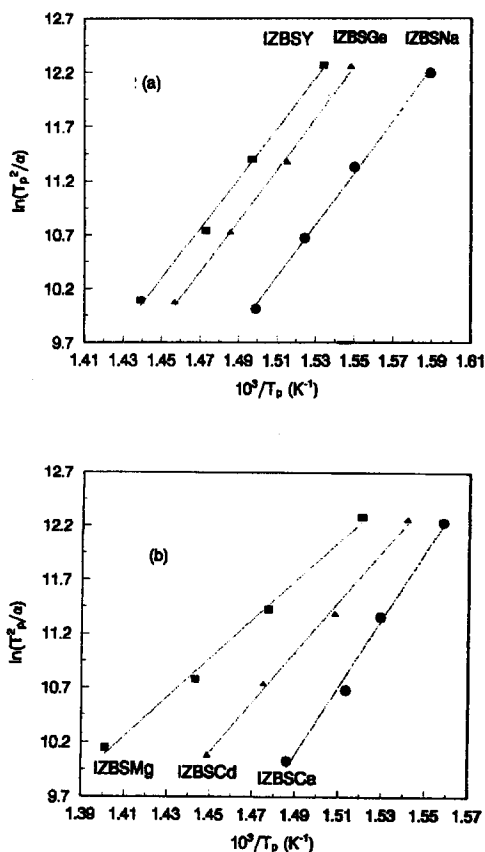


Fig. 2 Determination of the activation energy of crystallization by plotting $\ln(T_p^2/\alpha)$ vs $1/T_p$ for the substituted glasses (a) for IZBSNa, IZBSY, IZBSGe. (b) for IZBSCa, IZBSCd, IZBSMg

Table 2 Kinetic parameters $k(T)$ and $k_d(T)$ of substituted InF_3 glasses

$\alpha = 5^\circ\text{C min}^{-1}$					
Sample	$k(T_g)$	$k(T_p)$	$k_d(T_g)$	$k_d(T_x)$	$k_d(T_p)$
IZBSNa	$3.352 \cdot 10^{-3}$	0.303	$3.300 \cdot 10^{14}$	$4.331 \cdot 10^{14}$	$4.535 \cdot 10^{14}$
IZBSCa	$4.911 \cdot 10^{-4}$	0.382	$2.374 \cdot 10^{18}$	$3.886 \cdot 10^{18}$	$4.105 \cdot 10^{18}$
IZBSCd	$8.571 \cdot 10^{-4}$	0.244	$8.747 \cdot 10^{12}$	$1.423 \cdot 10^{13}$	$1.497 \cdot 10^{13}$
IZBSMg	$2.076 \cdot 10^{-3}$	0.190	$3.005 \cdot 10^9$	$4.617 \cdot 10^9$	$4.770 \cdot 10^9$
IZBSY	$1.028 \cdot 10^{-3}$	0.264	$7.541 \cdot 10^{12}$	$1.197 \cdot 10^{13}$	$1.263 \cdot 10^{13}$
IZBSGe	$9.991 \cdot 10^{-4}$	0.259	$3.109 \cdot 10^{13}$	$4.858 \cdot 10^{13}$	$5.105 \cdot 10^{13}$
$\alpha = 10^\circ\text{C min}^{-1}$					
Sample	$k(T_g)$	$k(T_p)$	$k_d(T_g)$	$k_d(T_x)$	$k_d(T_p)$
IZBSNa	$4.481 \cdot 10^{-4}$	0.569	$2.632 \cdot 10^{14}$	$3.601 \cdot 10^{14}$	$3.812 \cdot 10^{14}$
IZBSCa	$5.399 \cdot 10^{-4}$	0.633	$2.205 \cdot 10^{18}$	$3.683 \cdot 10^{18}$	$3.987 \cdot 10^{18}$
IZBSCd	$1.061 \cdot 10^{-3}$	0.531	$6.613 \cdot 10^{12}$	$1.155 \cdot 10^{13}$	$1.251 \cdot 10^{13}$
IZBSMg	$2.712 \cdot 10^{-3}$	0.351	$2.712 \cdot 10^9$	$4.282 \cdot 10^9$	$4.553 \cdot 10^9$
IZBSY	$1.556 \cdot 10^{-3}$	0.463	$6.345 \cdot 10^{12}$	$1.051 \cdot 10^{13}$	$1.111 \cdot 10^{13}$
IZBSGe	$1.335 \cdot 10^{-3}$	0.521	$2.310 \cdot 10^{13}$	$3.872 \cdot 10^{13}$	$4.121 \cdot 10^{13}$

In order to compare the tendencies to devitrification in this fluoride glass system, it is useful to point out that the crystal growth activation energy is usually equal to the viscous flow one, which decreases as the temperature is increased from T_g to T_l . This has been found to be true for some glasses [25]. Therefore, when a glass is heated in a DTA apparatus, devitrification occurs in the range of temperatures in which the number of nuclei formed and the crystal growth frequency factor are higher enough for the crystal growth kinetic barrier to be overcome. Thus, greater activation energies obtained from DTA should not necessarily be indicative of greater thermal stability.

Conclusion

A new criterion of $k_d(T)$ has been defined for the evaluation of glass stability from DTA measurements. It includes the kinetic parameters and critical temperatures. The new criterion is more accurate and reasonable than the existing criteria based on critical temperatures: $k(T_g)$ and $k(T_p)$. A high value of $k_d(T)$ means a poor stability of the glass. Study of the non-isothermal devitrification of the substituted InF_3 glasses at different heating rates and various temperatures has verified that the result of this new criterion $k_d(T)$ is affected neither by the

heating rate, nor by the temperature, while the results of the $k(T_g)$ or $k(T_p)$ criterion vary with the heating rates and temperatures. Among the six glass samples, $k_d(T)$ for the glass sample IZBSMg is lowest, so this glass composition is the most stable, while $k_d(T)$ for the glass sample IZBSCa is the highest, and this glass composition is the least stable. The stability sequence of these six substituted InF_3 glasses is IZBSMg>IZBSY>IZBSCd>IZBSGe>IZBSNa>IZBSCa. This result fits in well with the actual melting processes of the glasses.

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