

STUDY ON THE STABILITY OF GaF₃-BASED GLASSES BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

The glass formation and devitrification of GaF₃-based glasses were studied by differential scanning calorimetry. A comparison of various simple quantitative methods to assess the level of stability of multi-component fluoride glass systems is presented. Most of these methods are based on critical temperatures. In this paper a new parameter $k_b(T)$ is added to the stability criteria. The stability of several GaF₃-based glasses were experimentally evaluated and correlated with the activation energies of crystallization via this new kinetic criterion and compared with those evaluated by other criteria.

Keywords: DSC, GaF₃-based glasses, glass stability

Introduction

Fluoride-based glasses are being widely investigated because of their potential use as high-efficiency optical devices, e.g. fiber amplifiers, fast scintillators and up-conversion lasers [1–3]. Recently, it was found that the fluorogallate glasses have a potential application for infrared transmitting and active fibers because their phonon energy is lower than that of fluoroindates and their IR transmission range is larger than that of fluorozirconates [4]. However, improvements in fluorogallate glass stability and processing may be expected. For fluorogallate glass, potential applications related to optical fibers require that the devitrification problems during fiber drawing should be under control.

In this paper we study the glass stability of GaF₃-based system containing Al, Ba, Ca, Gd, Mg, Th and Zr fluoride by different simple quantitative methods [5–13], which are based on critical temperature [5–9], on the glass crystallization constant k [10, 11], and on the crystallization activation energy [12–13], respectively. These thermal parameters are easily and precisely obtained by means of DTA or DSC during the heating processes of glass samples. Dietzel [5] introduced the first glass criterion, thermal stability $\Delta T = T_c - T_g$. By using the critical temperatures, Hrubby [8] developed the Hr criterion,

$Hr = (T_c - T_g)/(T_m - T_c)$. On the basis of Hr criterion, Saad and Poulain [9] obtained other two criteria, the weighed thermal stability H' and S criteria, $H' = (T_c - T_g)/T_g$ and $S = (T_p - T_c)(T_c - T_g)/T_g$. Having compared the existing criteria based on critical temperatures, $k(T)$ criteria, and Branda's E/RT criterion, we consider synthetically both the kinetic parameters and characteristic temperatures and define a $k_b(T)$ stability criteria.

Experimental

Glass preparation

The starting materials were AlF₃, BaF₂, CaF₂, CdF₂, GdF₃, MgF₂, SrF₂, ThF₄, ZnF₂, ZrF₄ and Ga₂O₃. Gallium oxide was first fluorinated at 400°C with NH₄FHF in a platinum crucible. A batch of 10 g was mixed with excess ammonium bifluoride (NH₄FHF) as a precaution to convert trace oxide impurities to fluoride. Glasses were melted for 4–5 h in a platinum crucible with a resistance furnace, after complete melting, the glass melts were cast by pouring into open brass moulds. Glass samples were annealed at 300°C for 15 min. GaF₃-based glasses had the following mole composition formulae: 30GaF₃–25SrF₂–25CdF₂–15ZnF₂–MF_n (GSCZM), where MF_n is AlF₃, BaF₂, CaF₂, GdF₃, MgF₂, ThF₄ and ZrF₄.

Differential scanning calorimetry (DSC)

DSC scans were carried out by a CDR-1A Thermal Analyzer (SBIF, Shanghai) with an accuracy of ±0.5°C. For non-isothermal experiments, glass samples were heated from room temperature to 700°C at heating rates varying from 5 to 20°C min⁻¹. Bulk glass pieces (5–15 mg), which were water clear, instead of powder were used to avoid problems with particle size distribution, and Al₂O₃ powder was used as reference material.

Theoretical analysis

The relationship between crystallization fraction and the nucleation and growth rate is given by the Johnson–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:

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

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

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

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

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

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

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 peak of DSC curve, then ($T=T_p$):

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

After rearranging Eq. (5), Bansal *et al.* [14] developed a method for a non-isothermal analysis of devitrification. The final relation is as follows:

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

Therefore, a plot of the logarithm of the peak temperature squared divided by the heating rate, β , should be proportional to the reciprocal of T_p , with slope, E/R , and intercept, $\ln(E/R) - \ln v$. Then one can obtain E , v and $k(T)$. Surinach *et al.* [10] introduced a $k(T_g)$ criterion, and Hu and Jiang [11] developed the $k(T_p)$ criterion respectively:

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

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

Thus the values of these two parameters indicate the tendency of glass to devitrify on heating. The larger their values are, the greater the tendency is to devitrify. However, the formation of glass is a thermodynamic process and a kinetic process as well. A new criterion including both the kinetic parameters and characteristic temperature is being searched, and hoped to evaluate the glass stability over a broad temperature range. So, here, the Hr stable factor [8] is introduced to the $k(T)$, and define $k_b(T)$ criterion:

$$k_b(T) = v \exp(-HrE/RT) \quad (10)$$

where T is the temperature T_g , T_c or T_p . Just like the $k(T)$ criteria, the smaller the values of $k_b(T)$, are, the greater the thermal stability of the glass is. The obvious advantage of this method is that it can evaluate the glass stability over a broad temperature range, because it takes into account the inflexion point on the kink of the basic line, the first symptoms of crystallization occur and the appearance of the liquid phase [8].

Results and discussion

After preparing GaF₃-based glass samples, at first, the glass-forming ability, or the glass stability was estimated by a metallographic microscope. The observed results are listed in Table 1.

Table 1 Glass-forming ability of the GaF₃-based systems

Sample	Glass-forming ability
GSCZAl	the devitrification occurred in glasses
GSCZBa	one or two little isolated crystals in glasses
GSCZCa	several little isolated crystals in glasses
GSCZGd	the devitrification occurred in glasses
GSCZMg	few devitrification for glasses
GSCZTh	water clear
GSCZZr	water clear

From the DSC scans of GaF₃-based glasses, the characteristic temperatures such as the glass transition temperature, T_g , the onset crystallization temperature, T_c , the exotherm maximum temperature, T_p , and the melting temperature, T_m are given in Table 2. The stability of these seven GaF₃-based glass samples can be estimated by using these characteristic temperatures, T_g , T_c , T_p , T_m . The existing stability criterion parameters (ΔT , Hr , H' and S) based on these characteristic temperatures are shown in Figs 1a and 1b.

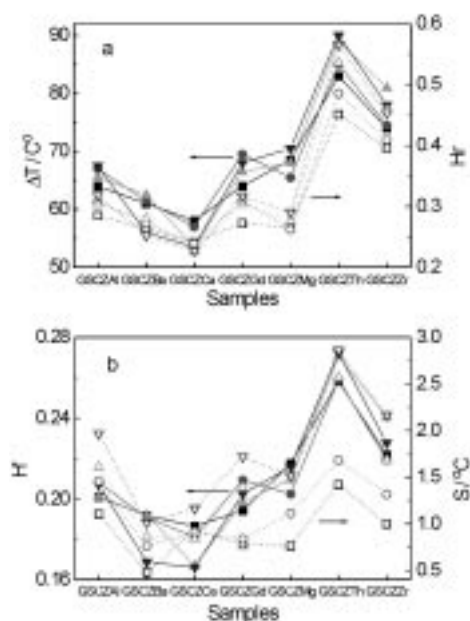


Fig. 1 The stable orders of the GaF₃-based glasses by (a) ΔT and Hr , (b) H' and S criteria (■ – 5°C min⁻¹, ○ – 10°C min⁻¹, △ – 15°C min⁻¹, ▽ – 20°C min⁻¹)

Table 2 Characteristic temperatures of the GaF₃-based glasses

Sample	$T_g/^\circ\text{C}$	$T_c/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_m/^\circ\text{C}$
	$\beta=5^\circ\text{C min}^{-1}$			
GSCZAl	318.5	382.5	388.0	612.5
GSCZBa	318.0	379.0	381.5	613.0
GSCZCa	311.0	369.0	374.0	614.5
GSCZGd	329.5	393.5	397.5	632.5
GSCZMg	315.0	383.5	387.0	645.0
GSCZTh	321.5	404.5	410.0	594.0
GSCZZr	333.5	407.5	412.0	599.0
$\beta=10^\circ\text{C min}^{-1}$				
GSCZAl	322.0	389.0	396.0	613.5
GSCZBa	322.5	384.0	388.0	614.0
GSCZCa	314.5	371.5	376.5	615.0
GSCZGd	332.0	401.5	405.5	630.0
GSCZMg	323.5	389.0	394.5	644.0
GSCZTh	328.0	413.0	419.5	594.5
GSCZZr	339.5	414.0	420.0	602.0
$\beta=15^\circ\text{C min}^{-1}$				
GSCZAl	325.5	391.0	399.0	614.5
GSCZBa	325.5	388.0	392.5	615.5
GSCZCa	320.5	374.0	379.0	616.0
GSCZGd	335.5	402.0	409.0	627.5
GSCZMg	324.0	392.0	399.0	645.5
GSCZTh	329.0	418.0	427.5	593.5
GSCZZr	337.0	418.0	425.0	602.0
$\beta=20^\circ\text{C min}^{-1}$				
GSCZAl	326.0	393.5	403.0	615.0
GSCZBa	332.0	388.0	394.0	616.0
GSCZCa	322.0	375.5	382.5	618.0
GSCZGd	336.0	404.0	412.5	627.0
GSCZMg	326.5	397.0	404.0	647.0
GSCZTh	330.5	420.5	431.0	590.0
GSCZZr	342.5	420.5	430.0	602.0

It is known that these criteria of glass stability allow a prediction of the tendency to devitrification. It is suggested that the higher values are, the higher the glass thermal stability should be. According to these suggestions, parameters, ΔT , Hr , H' and S

in Figs 1a and 1b show that the glass sample GSCZTh is the most stable in the seven samples. It is also found that GSCZZr is more stable than the other five glass samples and GSCZCa is the most unstable in the seven samples based on ΔT , Hr and H' at different heating rates. The stable order of these samples (except GSCZTh) changed with heating rates. According to Branda's criterion, E/RT_p , higher values of E/RT_p should be indicative of greater tendency to devitrify. GSCZTh is the most stable, and the stability orders at different heating rates are GSCZTh>GSCZZr>GSCZMg>GSCZAl>GSCZGd>GSCZBa>GSCZCa (Fig. 3b).

In order to compare the tendencies to devitrification in this fluoride glass system, it is useful to point out that the devitrification is a kinetic process, 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 $\ln(T_p^2/\beta)$ vs. $1/T_p$. The plots were found to be straight lines in accordance with Eq. (7). The slope E/R , and frequency factor ν are then evaluated by a least-squares fitting method. When the values of E/R and ν are known, the kinetic parameters can be calculated. The kinetic parameters $k(T)$ and $k_p(T)$ of GaF₃-based glasses are shown in Figs 3a–c.

Surinach *et al.* [10] and Hu and Jiang [11] suggested that the lower the value of $k(T_g)$ or $k(T_p)$ is, the higher the thermal stability of the glass should be. Accordingly, data on $k(T_p)$ in Fig. 3a indicate that the glass sample GSCZTh is the most stable and

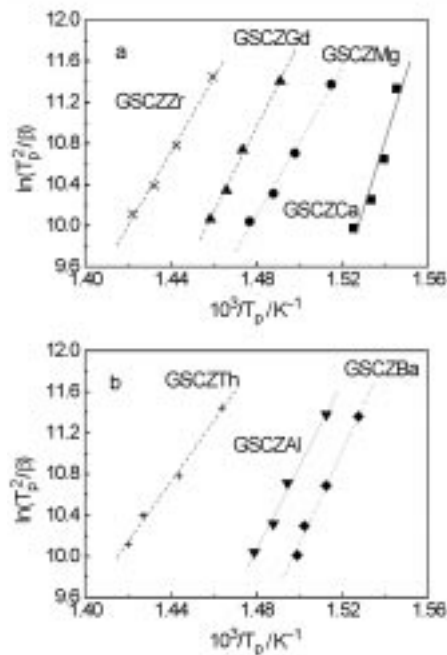


Fig. 2 Determination of the activation energy of crystallization by plotting $\ln(T_p^2/\beta)$ vs. $1/T_p$ for the GaF₃-based glasses: a – for GSCZCa, GSCZGd, GSCZMg, GSCZZr and b – for GSCZAl, GSCZBa, GSCZTh

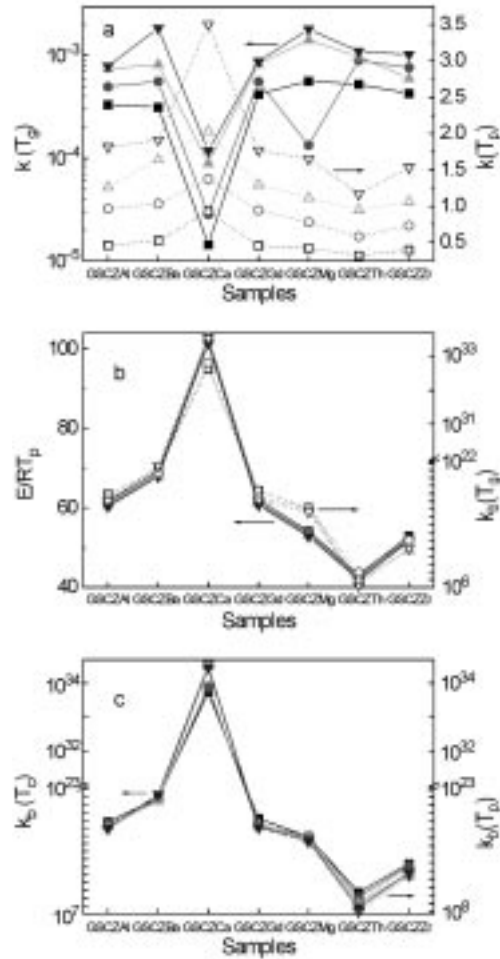


Fig. 3 The stable orders of the GaF₃-based glasses by a – $k(T_g)$ and $k(T_p)$, b – E/RT_p and $k_b(T_g)$, and c – $k_b(T_g)$ and $k_b(T_p)$ criteria (■ – 5°C min⁻¹, ○ – 10°C min⁻¹, △ – 15°C min⁻¹, ▽ – 20°C min⁻¹)

GSCZCa is the least stable of these glass samples at different heating rates. However, it is difficult to obtain the same stability sequence of GSCZAl and GSCZGd for GaF₃-based glasses by this criterion.

Surinach's criterion $k(T_g)$ is contrary to Hu's criterion $k(T_p)$ for this fluoride glass system shown in Fig. 3a and also does not accord with the actual melting process of the glass system. No consistent order of stability at different heating rates can be obtained (Fig. 3a). Therefore, this criterion does not fit for this glass system.

Data on $k_b(T_g)$, $k_b(T_c)$ and $k_b(T_p)$ in Figs 3b and 3c also show that the glass sample GSCZTh is the most stable, and the stability sequence is GSCZTh>GSCZr>GSCZMg>GSCZAl>GSCZGd>GSCZBa>GSCZCa at various heating rates. This

stability result agrees with that of the E/RT_p criterion (Fig. 3b) and the actual melting processes of GaF₃-based glasses.

According to Portier [15], ThF₄, ZrF₄ and AlF₃ as good glass formers are characterized by a high enthalpy of formation and a small ionic radius. These two features correspond to a strong metal-fluorine bond with certain covalence favorable to a polymerization in the liquid state. MgF₂ is a good structural intermediate [16]. It is able to participate in the continuous glass network and can increase the glass stability and chemical durability. BaF₂, CaF₂ and GdF₃ are glass modifiers in terms of the ratio of the standard heat of formation over the cationic radius [15]. According to Cottrant *et al.* [17], glass modifiers have two contradictory effects on glass formation in multicomponent system: 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, CaF₂, BaF₂ and GdF₃ have a higher tendency to crystallization. However, in the InF₃-ZnF₂-BaF₂-SrF₂ basic system, the addition of small quantities of GdF₃ (less than 4%) improves the stability [18].

Conclusions

A new criterion $k_b(T)$ has been defined for the evaluation of GaF₃-based glass stability from DSC data. It includes both the kinetic parameters and characteristic temperatures. The criterion is more accurate and reasonable than the existing criteria based on critical temperatures, ΔT , Hr , H' , S , and $k(T)$ criteria. A high value of $k_b(T)$ means poor stability of the glass. Study of the non-isothermal devitrication of seven GaF₃-based glasses at different heating rates and various temperatures has verified that the criterion $k_b(T)$ is neither affected by the heating rate, nor by the temperature, while the results of ΔT , Hr , H' , S , or $k(T)$ criterion vary with the heating rates and temperatures. Among seven glass samples, $k_b(T)$ of GSCZTh glass sample is the smallest, so this glass composition is the most stable. The stability order of these seven fluoride glasses is GSCZTh>GSCZZr>GSCZMg>GSCZAl>GSCZGd>GSCZBa>GSCZCa. This result fits in well with the actual melting processes of the glasses, and can also be explained by the correlation, which is the heat of formation of the compounds forming the glass and the ionic strength of the cations in the glass.

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