A REVIEW OF THE ROLE OF DSC ANALYSIS IN THE DESIGN OF FLUOROZIRCONATE GLASSES FOR FIBRE OPTIC APPLICATIONS

W. G. Jordan and A. Jha

Department of Materials Technology, Brunel University, Uxbridge, UB8 3PH, UK

Abstract

The relatively poor thermal stability of fluorozirconate glasses is a major factor preventing the realisation of their true potential for fibre optic applications. A range of methods based on both isothermal and non-isothermal DSC techniques, which can be employed to evaluate the thermal stability of fluorozirconate glasses, are described. The relevance of these thermal stability criteria to the design of fluorozirconate compositions capable of yielding high quality optical fibres is discussed.

Keywords: DSC, fluorozirconate glasses, kinetics, thermal stability

Introduction

Fluorozirconate glasses are receiving considerable interest due to their potential to outperform low-loss silica glass in fibre optic applications. The superior optical characteristics of fluorozirconate glasses can be attributed to their weak interionic bonding and the heavy mass of their constituent ions. Ironically, such intrinsic properties also result in relatively poor thermal stability. In order for high quality fluorozirconate optical fibres to be realised compositions must be designed which exhibit enhanced thermal stability whilst retaining their desirable optical properties.

Differential scanning calorimetry (DSC) analysis enables the thermal stability of fluorozirconate glasses to be evaluated using laboratory prepared specimens without the need for costly optical fibre fabrication trials. Several thermal stability parameters have been derived using the characteristic temperatures obtained from a single DSC scan [1, 2]. The kinetics of crystallisation have been studied using a number of methods [3-6] based on the Avrami equation [7].

Experimental time-temperature-transformation (*TTT*) curves have been constructed using isothermal heating techniques [8] and critical cooling rates for glass formation subsequently determined. The relationship between the thermal stability of fluorozirconate glasses and the recently reported correlation be-

tween the width of the glass transition region measured by DSC and the temperature dependence of glass melt viscosity [9] has also been investigated.

Based on the above DSC analysis a set of thermal stability criteria has been outlined which if satisfied indicates fluorozirconate glasses that can be readily worked into a fibre geometry. It should be noted that the primary aim of all the DSC techniques discussed in this paper is to evaluate the intrinsic thermal stability of fluorozirconate compositions. The realisation of high quality optical fibres also requires the careful control of extrinsic factors such as moisture contamination and impurities which can act as heterogeneous nucleation sites during optical fibre fabrication.

Table 1 Fluorozirconate glass-forming compositions (mole%)

Acronym	ZrF_4	BaF_2	LaF_3	AlF_3	YF3	InF_3	LiF	NaF	CsF
ZBL	64	32	4	–	–	–	–	–	–
ZBLA	62	30	4	4	–	–	–	–	–
ZBLAL	52	20	4	4	–	–	20	–	–
ZBLAN	52	20	4	4	–	–	–	20	–
ZBLYINC	52	20	4	–	2	2	–	10	10

Fluorozirconate glass optical fibres

ZrF_4 is the major constituent in fluorozirconate glasses and acts as a conditional network-former when combined with BaF_2 which is a network-modifier. Network-stabilising fluorides such as LaF_3 [10] and AlF_3 [11] enhance the glass-forming ability of fluorozirconate compositions. Similarly, the addition of the monovalent network-modifying fluorides NaF and LiF [12] results in further improvements in glass formation. Of the many fluorozirconate glasses designed the ZBLAN composition [13] is receiving the greatest interest. The compositions and associated acronyms for some of the more widely studied fluorozirconate glasses are given in Table 1. The fabrication of fluorozirconate optical fibres is a costly process and involves the glass passing through the thermal range of instability on two separate occasions. The first arises when the melt is quenched to form a preform and the second occurs due to reheating of the preform for fibre drawing. Hence, evaluation of the crystallisation tendency of fluorozirconate glasses on both cooling and heating is essential so that compositions can be optimised in this respect prior to optical fibre fabrication.

Thermal stability parameters

Numerous thermal stability parameters have been proposed based on the glass transition (T_g), onset of crystallisation (T_x), peak crystallisation (T_P), and melting (T_m) temperatures obtained from a single non-isothermal DSC scan such as that shown in Fig. 1.
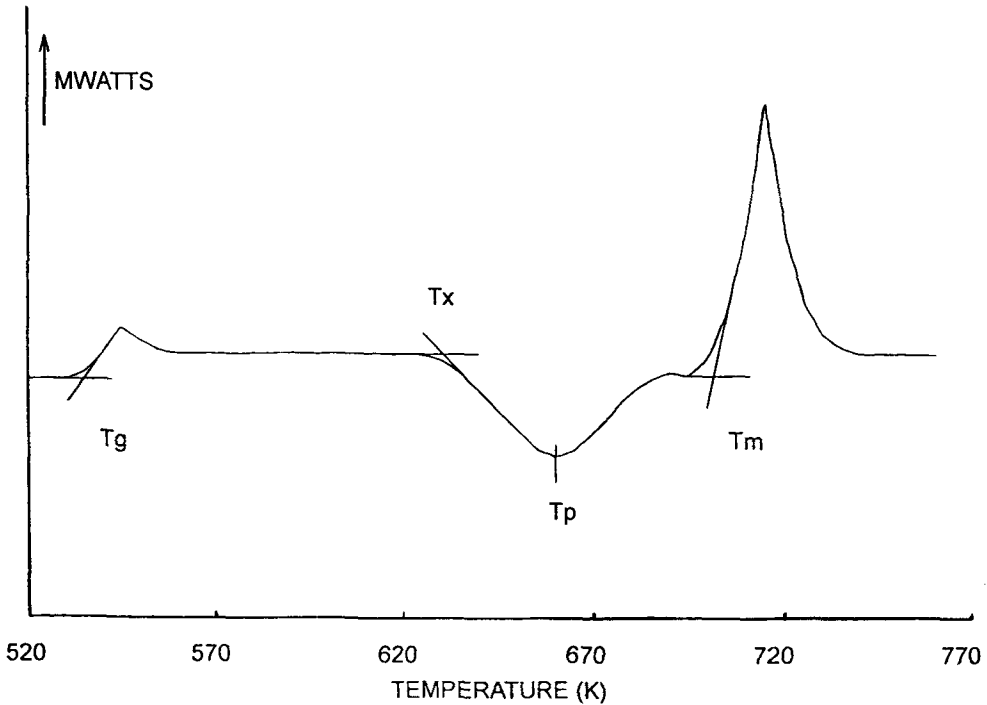

Fig. 1 Non-isothermal DSC scan for ZBLAN glass heated at 10 deg·min^{-1}

The three most widely used stability parameters employed in the design of fluorozirconate glass-forming compositions are defined as follows:

$$\Delta T = (T_x - T_g) \tag{1}$$

$$H_R = (T_x - T_g) / (T_m - T_x) \tag{2}$$

$$S = (T_x - T_g)(T_p - T_x) / T_g \; (^\circ C) \tag{3}$$

ΔT gives an indication of the devitrification tendency of a glass when heated above T_g and defines the temperature range in which optical fibres can be drawn

from preforms. A large ΔT value is desirable since such glasses are unlikely to crystallise during the fibre drawing process. Similarly, large values of H_R [1] and S [2] imply that a glass is less susceptible to crystallisation when heated above T_g. At this stage, the nucleation and crystal growth equations for the condition of fibre drawing should be considered.

The equation for volume homogeneous nucleation rate (I_v) based on classical nucleation theory can be written in the form:

$$I_v = A\exp[-(\Delta G^* + Q_c)/kT]\qquad(4)$$

where A is a pre-exponential term, ΔG^* is the thermodynamic barrier, Q_c is the kinetic barrier, k is Boltzmann's constant and T is temperature. Equation (4) is governed by the kinetic term Q_c which decreases exponentially with increasing ΔT. This is the reason why the width of the T_x-T_g gap provides a good indication of resistance to nucleation and hence glass stability. The crystal growth rate (U_c) can be expressed as follows:

$$U_c = [\Delta S_m / 6(\pi a_o)^2]\,1/n\,[(\Delta T_r)^2/T]\qquad(5)$$

where ΔS_m is the entropy of melting, a_o is the mean atomic or ionic diameter for a diffusive jump, n is the melt viscosity and ΔT_r is a measure of the undercooling sustained by a melt ($\Delta T_r = (T_m-T)/T$). If we consider the condition $T = T_x$ it can be seen from Eq. (5) that the crystal growth rate falls rapidly as the T_m-T_x difference decreases. The incorporation of this term in the H_R parameter makes it a more comprehensive indication of glass stability since the numerator defines the nucleation rate and the denominator the growth rate. The inclusion of T_P-T_x in the S parameter provides further information on crystal growth with wider devitrification exotherms indicating slower crystallisation rates.

Table 2 Thermal stability parameter data ($\beta = 10$ deg·min^{-1})

Acronym	T_g / K	T_x / K	T_p / K	T_m / K	ΔT / K	H_R	S / °C
ZBL	588	663	671	783	75	0.63	1.90
ZBLA	584	664	683	786	80	0.66	4.89
ZBLAL	522	615	632	750	93	0.68	6.35
ZBLAN	533	625	644	715	92	1.02	6.72
ZBLYINC	546	636	657	725	90	1.01	6.92

The characteristic temperatures and thermal stability parameters for a range of fluorozirconate glasses are given in Table 2. Employing the evaluation of ΔT, H_R and S is a quick and easy method for assessing thermal stability. However,

the limitations of such techniques must be fully appreciated. Inconsistencies exist in the predictions made by the parameters listed in Table 2. Moreover, the parameters are in essence indications of resistance to devitrification on heating and hence only apply to the fibre drawing process. They provide relatively little information on a composition's ability to produce crystal-free glass preforms.

Kinetics of crystallisation

Several methods have been proposed to study the crystallisation kinetics of fluorozirconate glasses based on the Avrami equation [7]:

$$X = 1 - \exp(- kt)^n \qquad (6)$$

where X is the fraction crystallised, k is a factor related to nucleation and crystal growth rates, t is time and n is a dimensionless quantity termed the Avrami exponent. The temperature dependence of k over a limited range is given by the Arrhenius relationship:

$$k = k_o \exp(- E_c / RT) \qquad (7)$$

where k_o is a frequency factor, E_c is the apparent activation energy for crystallisation and R is the universal gas constant. It can be seen from Eqs (6) and (7) that the devitrification process appears to be governed by the kinetic parameters E_c and n. The Ozawa-Chen equation [3, 4] enables the evaluation of E_c from the shift in T_P to higher temperatures with increasing heating rate (β) in accordance with the Kissinger method [14]:

$$\ln(T_p / \beta) = E_c / RT_p + (1 / n) \ln[- \ln(1 - X)] - \ln(k_o / 2) \qquad (8)$$

Plotting $\ln(T_P/\beta)$ vs. $1/T_P$ yields a straight line with a gradient equal to E_c/R. A similar approach has been reported by Augis and Benett [5]:

$$\ln(Tp^2 / \beta) = E_c / RT_p + \ln(E_c / R) - \ln(k_o) \qquad (9)$$

Equation (9) predicts that the relationship between $\ln(Tp^2/\beta)$ and $1/T_P$ is linear with a slope of E_c/R. MacFarlane et al. [6] proposed an alternative equation based on the diffusion mechanisms involved in devitrification:

$$\ln(\beta) = - E_c / RT_p + Nk' - \ln[- \ln(1 - X)] \qquad (10)$$

where N is the number of nuclei and k' is a diffusion related constant. Plotting $\ln(\beta)$ vs. $1/T_P$ yields a straight line with a gradient of $-E_c/R$. A representative plot for a ZBLAN glass using the Ozawa-Chen approach is shown in Fig. 2.
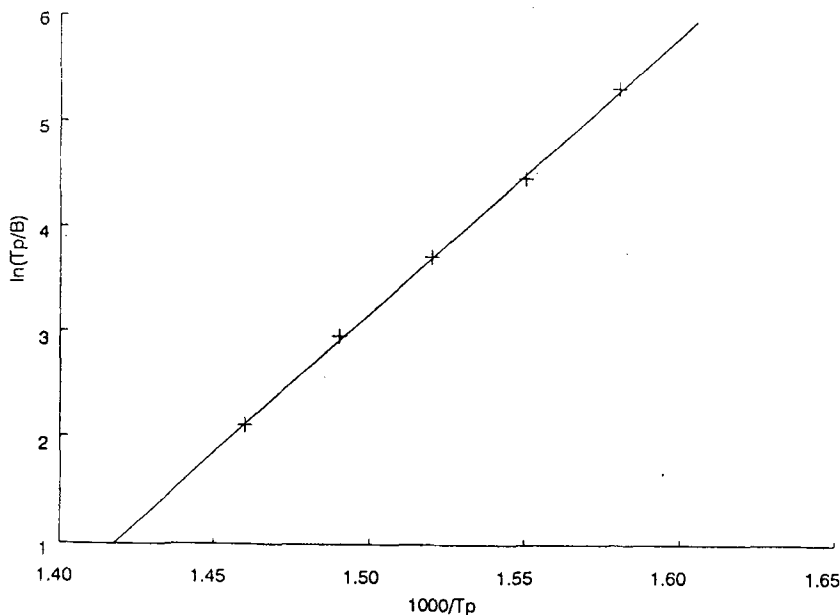

Fig. 2 Evaluation of E_c for ZBLAN glass using the Ozawa-Chen approach

Once E_c has been determined n can be evaluated using the relationship proposed by Piloyan et al. [15]:

$$nE_c / R = d[\ln(\Delta Y)] / d(1 / T) \tag{11}$$

where ΔY is the displacement of the non-isothermal DSC trace from the base line. Plotting $\ln(\Delta Y)$ vs. $1/T$, as illustrated in Fig. 3, gives a straight line with a slope of nE_c/R from which n can be calculated. The E_c and n values for a range of fluorozirconate glasses are summarised in Table 3. It can be seen from Table 3 that the various methods of evaluating E_c are in good agreement. The n values were obtained from 10 deg·min^{-1} non-isothermal DSC scans using the E_c values from Eq. (8). The Avrami exponents are all close to 3 which implies three-dimensional crystal growth from a constant number of nuclei [16].

Experimental results suggest that lower E_c values correspond to more thermally stable glasses. At present, the theoretical explanation for this is rather nuclear but is believed to stem from the close relationship between E_c and the shear viscosity activation energy (E_n). A low E_n value implies that a glass will

remain highly viscous at working temperatures significantly greater than T_g. If this effect persists in the vicinity of T_x the devitrification process will be inhibited. A low n value is also indicative of good thermal stability. Our experience with a number of fluorozirconate compositions suggests that glasses which exhibit a wide devitrification exotherm and hence a slow crystallisation rate also have relatively low n values.
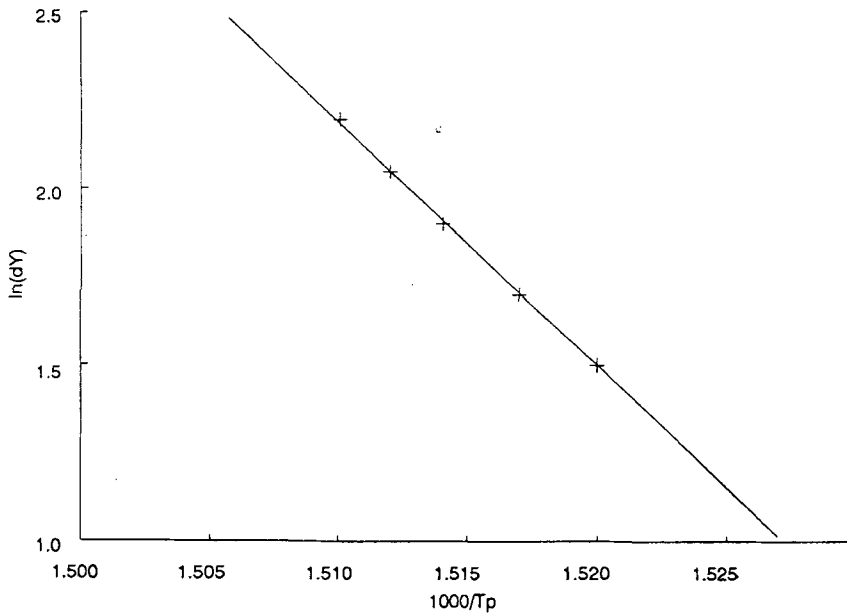

Fig. 3 Evaluation of n for ZBLAN glass

Table 3 Kinetics of crystallisation data ($\beta = 10$–160 deg·min^{-1})

Acronym	E_c / kJ·mol^{-1} Eq.(8)	E_c / kJ·mol^{-1} Eq.(9)	E_c / kJ·mol^{-1} Eq.(10)	n
ZBL	317	315	315	3.5
ZBLA	312	312	310	3.4
ZBLAL	172	168	171	3.1
ZBLAN	195	194	195	2.9
ZBLYINC	159	156	158	3.0

Critical cooling rates for glass formation

The relationship between the time required for a fixed rate of crystallisation as a function of temperature and glass-forming ability was first proposed by

Uhlmann [17]. For $X \ll 1$ the Johnson-Mehl-Avrami equation [18, 7] can be used to estimate the volume fraction of crystals formed (X) in time (t):

$$X \approx (1 / 3)\pi I_v U_c^3 t^4 \qquad (12)$$

where I_V is the homogeneous nucleation rate per unit volume and U_c the three-dimensional crystal growth rate. Equation (12) describes a time-temperature-transformation (TTT) curve which can be constructed using data obtained from isothermal DSC scans [8].

The glass specimens are first melted and then rapidly cooled (100–200 deg·min^{-1}) to the isothermal hold temperature. Once thermal equilibrium is reached the crystallisation event is monitored and then the process repeated for different temperatures. Each DSC scan provides a value of T_P which corresponds to a specific time and temperature. If it is assumed that the volume fraction crystallised is constant when $T = T_P$ the TTT curve can be constructed from the data obtained. Although this assumption is not strictly valid for all amorphous materials, in the case of the fluorozirconate glasses it provides a good approximation. The critical cooling rate for glass formation (R_c) can be estimated from the TTT curve via the following equation:

$$R_c = (T_m - T_N) / t_N \qquad (13)$$

where T_N is the temperature at the nose of the TTT curve and t_N the corresponding time. The TTT curve for a ZBLAN glass is illustrated in Fig. 4 and the R_c values for a range of fluorozirconate glasses summarised in Table 4. The critical cooling rates reported in Table 4 are consistent with experimental observations, the more thermally stable glasses being those with lower R_c values. The major advantage of this approach is that it enables the study of crystallisation on cooling and hence gives an indication of whether or not a fluorozirconate glass composition can produce high quality optical fibre preforms. An alternative method for determining R_c has been proposed by Barandarian et al. [19]. This technique involves melting the glass and then measuring the value of T_P at different cooling rates (β). R_c is subsequently determined by an extrapolation of the fitting of the T_P values with the following expression:

$$\ln(\beta) = A - B / \Delta T_c^2 \qquad (14)$$

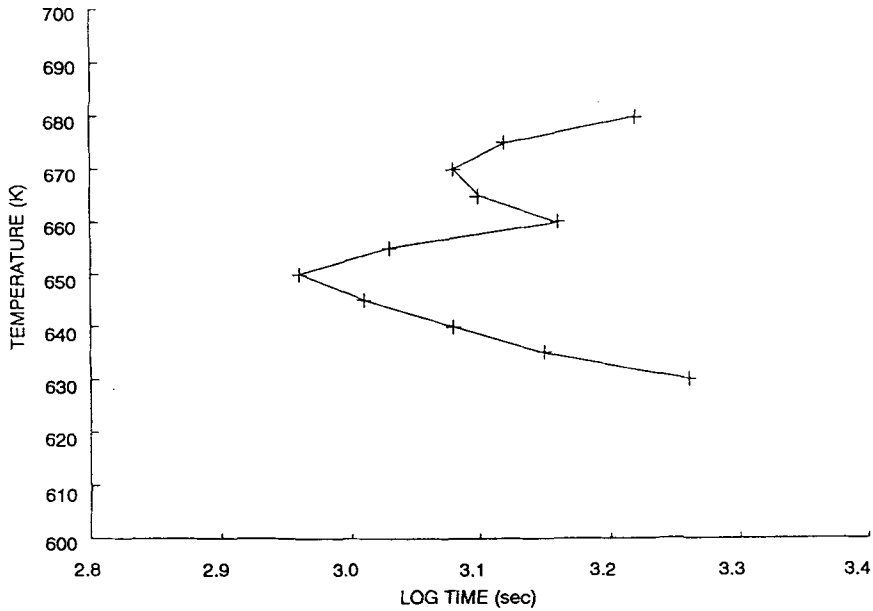where ΔT_c is the undercooling and $A = \ln(R_c)$ when ΔT_c increases to infinity.

Fig. 4 Experimentally constructed *TTT* curve for ZBLAN glass

Table 4 Critical cooling rates for fluorozirconate glasses

Acronym	R_c / deg·min^{-1}
ZBL	300.21
ZBLA	60.44
ZBLAL	32.76
ZBLAN	4.20
ZBLYINC	8.00

Viscosity working range predictions

A correlation between the width of the glass transition region on heating measured by DSC and the shear viscosity temperature dependence of fluorozirconate glasses has been established by Moynihan [10]:

$$C = (\Delta H^* / R)\Delta(1 / T_g) = (\Delta H^* / R)[(1 / T_g) - (1 / T_{gi})] \qquad (15)$$

where C is termed the Cooper constant, ΔH^* is the shear viscosity activation enthalpy and T_{gi} is the extrapolated completion temperature of the glass transition as defined in Fig. 5.
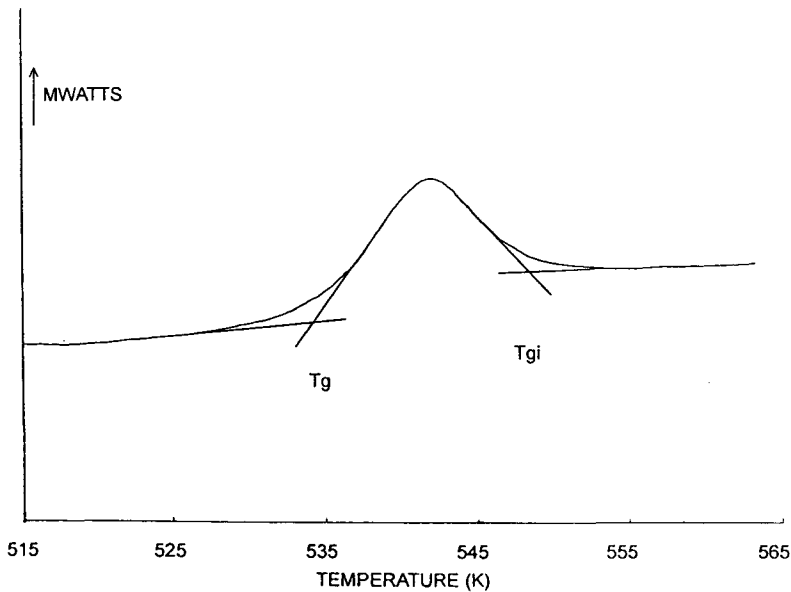
Equation (14) is only valid if the cooling to heating rate ratio is within the rough range $0.2 \leq |\beta_C/\beta_H| \leq 5.0$. Consequently, it is recommended that glass specimens are initially heated up to T_g at $\beta_H = 10$–20 deg·min^{-1} and then cooled at $\beta_C = 10$–20 deg·min^{-1} to erase the original thermal history prior to recording a DSC scan. Combining the correlation between the width of the glass transition region and shear viscosity with the Fulcher equation and invoking the observations made by Angell [20] enables the viscosity of a glass at a given temperature to be estimated via the following equation:

$$4\lg n = -5 + 14.2 / [\{0.147(T - T_{gi}) / T_{gi}^2 \Delta(1 / T_g)\} + 1] \qquad (16)$$

The viscosity of a fluorozirconate glass should be within the rough limits $5 \geq \lg n(\text{Pas}) \geq 3$ in order for it to be drawn into fibre [21]. The temperatures which correspond to these limits can be determined using Eq. (16). The working ranges for a series of fluorozirconate glasses are summarised in Table 5.

The optical fibre drawing process is usually carried out at a temperature in the middle of the working range (T_w). The viscosity at T_w and the parameter $T_x - T_w$ have also been included in Table 5. A large $T_x - T_w$ value indicates glasses for which the onset of crystallisation is far removed from the working temperature, and which are therefore less susceptible to devitrification during fibre drawing.

Table 5 Optical fibre drawing parameters

Acronym	Working range / K	$\lg n$ (Pas) at T_w	$T_x - T_w$ / K
ZBL	639–671	3.89	8
ZBLA	638–675	3.89	8
ZBLAL	585–625	3.89	10
ZBLAN	592–629	3.90	15
ZBLYINC	605–642	3.90	13

Discussion

The thermal stability parameters predict an increase in resistance to devitrification on heating when trivalent fluorides and monovalent fluorides are incorporated in fluorozirconate glass compositions. The kinetic parameters E_c and n exhibit a similar trend. The incorporation of trivalent fluorides also dramatically reduces the critical cooling rate for glass formation. The addition of NaF gives rise to a further significant reduction in the value of R_c. From the data available it appears that trivalent fluorides and NaF are essential components in fluorozirconate compositions capable of forming crystal-free glass preforms.

Table 6 Thermal stability criteria for high quality optical fibres

ΔT / K	H_R	S / °C	E_c / kJ·mol^{-1}	n	R_c / deg·min^{-1}	$T_x - T_w$ / K
≥ 90	≥ 1.0	≥ 6.5	≤ 200	≤ 3.0	≤ 20.0	≥ 10

The T_x–T_w values evaluated via viscosity considerations follow a similar trend to the ΔT thermal stability parameter. This is not suprising due to the close relationship between T_w and T_g. In general, the various thermal stability criteria discussed are consistent in their prediction of the more stable fluorozirconate compositions. However, in order to characterise the crystallisation behaviour fully, a range of thermal stability characteristics should be determined. The set of thermal stability criteria listed in Table 6 has been developed using DSC analysis and experimental observations and if satisfied is believed to indicate fluorozirconate compositions capable of producing high quality optical fibres.

Conclusions

DSC analysis enables the thermal stability of fluorozirconate glasses to be evaluated without the need for the costly fabrication of optical fibres. The data produced provides valuable information for the design of fluorozirconate compositions capable of yielding high quality optical fibres.

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Zusammenfassung — Die relative schwache thermische Stabilität von Fluorozirkonaten ist einer der Hauptfaktoren für die Verhinderung der Anwendung ihres vorhandenen Potentiales für Glasfaseranwendungen. Es wurde eine Reihe von Methoden, basierend sowohl auf isothermen als auch auf nichtisothermen DSC-Techniken, beschrieben, die zur Feststellung der thermischen Stabilität von Fluorozirkonat-Gläsern verwendet werden können. Weiterhin wird die Relevanz dieses thermischen Stabilitätskriteriums für die Planung von Fluorozirkonatzusammensetzungen beschrieben, die eine Fertigung von hochwertigen Glasfibern ermöglichen.