THE INFLUENCE OF REACTIVE ATMOSPHERE PROCESSING ON THE CRYSTALLISATION KINETICS OF GaF$_3$/InF$_3$ BASED GLASSES

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ABSTRACT

Gallium-indium fluoride based glasses are known as one of the lowest phonon energy hosts for Pr-ions. However, to date the fabrication of low background loss fibres have been proved difficult. In the present investigation, GaF$_3$/InF$_3$ based glasses are prepared under the controlled reactive atmosphere of SF$_6$, HF and N$_2$ gas mixture. The devitrification characteristics for different reactive-atmosphere (RA) treatment have been studied using differential scanning calorimetry. From the isothermal data, the time-temperature-transformation curves have been constructed and on this basis, the improvement in glass stability is discussed. Measured fibre loss results from glasses prepared under RAP are also discussed in the context of impurities present in the melt.

1.   INTRODUCTION

In recent years, gallium and indium fluoride (GaF$_3$/InF$_3$) multicomponent glasses[1] have been developed for their applications as a host for Pr-ions for the second window amplifier, as passive fibres for CO lasers and for fibre sensors. The application of group IIIA fluoride glasses as a promising low phonon-energy host (500 Rcm^{-1}) for Pr-ions requires fibres of low background loss (α_T). The value of α_T depends on both the intrinsic and extrinsic factors. The intrinsic factors such as multiphonon and uv absorptions and Rayleigh scattering are limited by the physical and optical properties of the host materials whereas the extrinsic factors are dependent on the extrinsic absorption and scattering. In Pr-doped fibre amplifier, the signal gain depends on the pump power and the lifetime of the metastable $^1G_4$ level. Both of these factors are detrimentally affected by the overall impurity absorption and their concentration. The high-energy impurity phonons shorten the lifetimes of $^1G_4$ level in Pr-ion. In designing fibre amplifier, it is also of paramount importance that neither the pump nor the signal band should overlap with the impurity bands. The reduction in the overall impurity concentrations in GaF$_3$ glass is also important for developing robust power transmission cable and for fibre sensors in which the sensing window should not be obscured by the impurity bands. The number of crystallites as extrinsic scattering centres should be minimized in all fibre applications as they can not only contribute to overall fibre background loss but also adversely affect the fibre strength[2].

The origin of scattering centres and extrinsic absorption in gallium and indium

fluoride glasses lies in the chemical purity of starting powder. Both gallium and indium, like their aluminium analogue, are very reactive metals and the oxides are their preferred stable compounds at low and high temperatures. The fluorides are made either via direct fluorination of metal which is kinetically a slow process or via an aqueous route. In the aqueous route[3], the metal is dissolved into a nitric acid solution from which either a mixture of oxyfluoride and GaF$_3$ or an oxide is precipitated. From the mixture of GaF$_3$ and GaOF, gallium fluoride is subsequently purified by vacuum sublimation process. Whereas the oxide is tightly fluorinated with ammonium hydrogen bifluoride in the temperature range of 250° to 400°C for several hours. The purification process, being a gas-solid reaction, is very much dependent on the kinetic factors and the reactor geometry. A discussion on these kinetic factors and reaction design is beyond the scope of this paper.

In the present investigation, we have analyzed the influence of different types of fluorinating atmospheres on the devitrification characteristics of the gallium-indium fluoride glasses. The devitrification has been studied by differential thermal analysis technique and the results of transformation kinetics are discussed in view of the role of fluorinating atmosphere on glass stability. The glass rods were also cast and these were subsequently drawn into fibres. The measured fibre loss data are also reported.

2.   EXPERIMENTAL PROCEDURE

For making gallium-indium fluoride glass containing 20 mole % GaF$_3$, 15 mole% InF$_3$, 30 mole% PbF$_2$, 20 mole% CdF$_2$ and 15 mole% ZnF$_2$, the constituent fluoride compounds in the powder form were mixed inside a dry nitrogen atmosphere glove box. Each powder mixture was then heat treated in a prespecified reactive atmosphere for a short and a long duration at low and high temperatures respectively. The conditions for reactive atmosphere processing (RAP) are listed in **Table 1**. The HF gas was premixed with nitrogen and the mixture composition was 97.5% N$_2$ and 2.5 HF. This gas mixture in table 1 shown below is designated as "HF". The dilution of HF gas with the carrier nitrogen gas was proved to be essential for preventing the rapid degradation of silica glassware used for designing RAP apparatus. In the composition GaF6, the addition of ZnF$_2$ was made at the end of RA treatment prior to melting.

The RA treated powders were rapidly transferred inside a dry nitrogen atmosphere maintained glove box for melting and casting. The melting furnace was maintained at 825°C and the time for melting plus homogenization in dry nitrogen atmosphere was deliberately limited to 45 minutes. This was ensured in order to minimize the residual moisture and oxygen pick up by the fluorogallate melts while dwelling inside the melting chamber in the glove box. After 45 minutes at 825°C, the melt was cast into a preheated brass mould at 225°C and swiftly transferred inside the annealing furnace in the glove box. The glass annealing was carried out at 225°C for 8 hours and then the furnace was switched off to allow slow cooling of the annealed glass. A 25-35 mg size broken glass fragment from each of the annealed samples was taken for thermal analysis. The characteristic temperatures obtained at 20°C per minute isochronal rate are reported in **Table 2**.

3.   RESULTS

The characteristic temperatures such as the onset of glass transition, T$_g$ and crystallization, T$_x$ and the peak of crystallization, T$_p$ for various glasses are reported in **Table 2**. From these measured data, the values of glass stability parameters, $\Delta T = T_x - T_g$ and S =

$(T_x-T_g)(T_p-T_x)/T_g$ are derived. A large value of ΔT is a strong indicator of good glass stability. In the present situation, the narrowest and the widest ΔT values are reported in **Table 2**. The powder mixtures without RAP treatment failed to produce glass and therefore in Table 1, we do not have a set of comparable characteristic temperatures for a glass derived from chemically untreated powder mixture. Occasionally glasses in very thin sections were produced from such untreated melts. However, these were not thought to be representatively similar to 8mm (diameter) by 60 mm (long) rod sections of clear and transparent glass reported above. **Figure 1** compares the isochronal thermograms (20°C/minute) of RAP glass samples from which it is evident that the shape of the devitrification exotherm is dependent on the RAP condition. In particular, the 19 hour long SF_6 treatment at 600°C has a major influence on the breadth of the exotherm. The breadth of each exotherm is defined by the S parameter and these are also listed in **Table 2**. The larger the value of S parameter, the greater the resistance of the vitreous phase against crystallization. On this basis, the sample GaF3 appears to be the most stable. All bulk glass samples listed above were clear and transparent in appearance except GaF2 which was cast into a 8 mm diameter by 60 mm long rod and in the core of this rod, a streak of crystals grew along the rod axis during melt solidification. Thermal analysis was carried out by taking the clear glass sample from the surface of the rod.

Table 1: **Description of reactive atmosphere processing conditions.**
N_2 **flow rate = 5 litre.min^{-1}. SF_6 flow rate = 200 ml.min^{-1} and (97.5 vol% N_2 + 2.5 vol% HF) = 200 ml.min^{-1}.**

N°	Description of RAP treatment	Processing time and temperature	
		Temperature, °C	Time, hours
GaF1	SF_6 + N_2 gas mixture	600	19
GaF2	NH_4FHF + N_2 gas	350 + 550	3 + 2
GaF3	HF + N_2 SF_6 + N_2	350 + 375 600	3 + 5 19
GaF4	HF+SF_6+N_2	400	19
GaF5	HF+SF_6+N_2 SF_6+N_2	600 600	3 19
GaF6	HF+SF_6+N_2 SF_6+N_2	600 600	3 19

The exotherm from each thermogram shown in **Figure 1** was area integrated and from the values of fractional area, the fractional volume fraction crystallized, X, was determined. The value of X was plotted against time 't' in seconds and these plots are compared in **Figure 2** and are known as the rate of transformation curves. The period of induction (τ_o, s) for each transformation curve was determined by finding the point of intersection of linearly extrapolated section of the tail at low volume fractions (X<0.05) and the linear steady state rate between X=0.2 and 0.7. The approximate derived values of τ_o for above-listed glasses GaF1 to GaF6 are compared in **Table 2**. Isothermal transformation rate data,

as shown in **Figure 2**, were obtained at different temperatures between T_x and T_p for constructing the time-temperature-transformation (t-t-t) curve for each glass and these are compared in **Figure 3** for the volume fraction of crystal transformed, $X = 10^{-3}$. The delay in the transformation process, as indicated by the right hand shift of the t-t-t curve, compares well with the data for long period of induction, τ_0 in **Table 2**. For glass GaF_3 however the period of induction is significantly smaller than the relative delay in the phase transformation process as indicated by the t-t-t curve.

Table 2: **Measured characteristic temperatures of RAP glasses. Isochronal heating rate = 20°C per minute.**

N°	Characteristic Temperatures, °C			Stability parameters	
	$T_g \pm 2$	$T_x \pm 2$	$T_p \pm 2$	ΔT	$S, °C/\tau_0, s$
GaF1	257	344	351	87	2.4/ ~70
GaF2	256	343	356	87	4.4/ ~90
GaF3	255	343	358	88	4.5/ ~65
GaF4	258	333	337	75	1.2/ ~35
GaF5	261	348	367	87	6.3/ ~135
GaF6	260	354	365	94	4.0/ ~130

Cast glass rods (GaF1, GaF4 and GaF6) were also drawn into fibres and the measured total loss for three types of fibres are compared in **Figure 4**. The glass rod surface was not polished prior to fibre drawing. It is anticipated that the surface defects also contributed to the overall fibre loss together with the extrinsic absorption due to the transition metal impurities. The fibre with the highest loss was derived from glass having over 2000 ppmw of analyzed oxygen whereas the loss less than 10 dB/m was obtained from glass rods containing less than 1000 ppmw of oxygen. The lowest loss fibres drawn to date had a total oxygen concentration less than 700 ppmw. Another contributory factor to the total loss was also due to transition metal impurities in GaF_3/InF_3 glasses.

4. DISCUSSION

The measured loss values in multimode unclad fibres (~ 135 μs) appear to be in good agreement with the analyzed oxygen content of the cast glass. It is also evident from the comparison of the stability data that the high temperature RAP with SF_6 gas enhances the resistance of GaF_3 glass against devitrification. The use of SF_6 as an RAP gas is important in determining the overall concentration of dissolved oxygen as oxyfluoride and cadmium oxide (from CdF_2). At elevated temperature, GaF_3 forms from GaOF by reacting with SF_6 gas: $2GaOF + SF_6 = 2GaF_3 + F_2 + SO_2$. A similar redox reaction with gallium oxide is also possible. Note that the use of HF alone will produce H_2O gas which is less stable at high temperatures than SO_2. Therefore the removal of oxygen from powder will be adversely affected when HF is only used as a reagent gas for removing oxygen. SO_2 is comparatively more stable gas and lowers the chemical potential of oxygen more than H_2O as a reaction

product in the forward direction. As a result, the reduction in oxygen concentration is larger with the use of SF_6 gas than with HF alone. A mixture of these two gases always yields better quality glass.

5. CONCLUSIONS

The rate of devitrification of GaF_3 glass is dependent on the RAP treatment condition which determines the residual concentration of oxygen in the cast glass rods. The multimode unclad fibre loss is also connected with the residual oxygen concentration in the glass. The lowest loss figures in multimode (100-135μm) fibres of 1-2 metre in length varies 12 dB/m and 5 dB/m at 500 nm and 1300 nm respectively.

6. References:

[1]. A Soufiane: PhD thesis, University of Rennes, Rennes, 1992.
[2]. S G Carter: In Fluoride Glass Optical Fibres, ed.P W France, Blackie, 1990, P.241.
[3]. B E Kinsman, A Jha and M Poulain, Int. EU/RACE project report, July 1994, P.3.
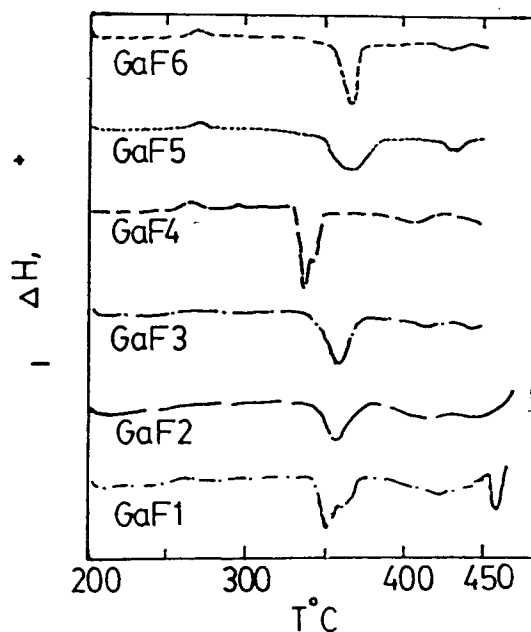
Acknowledgments

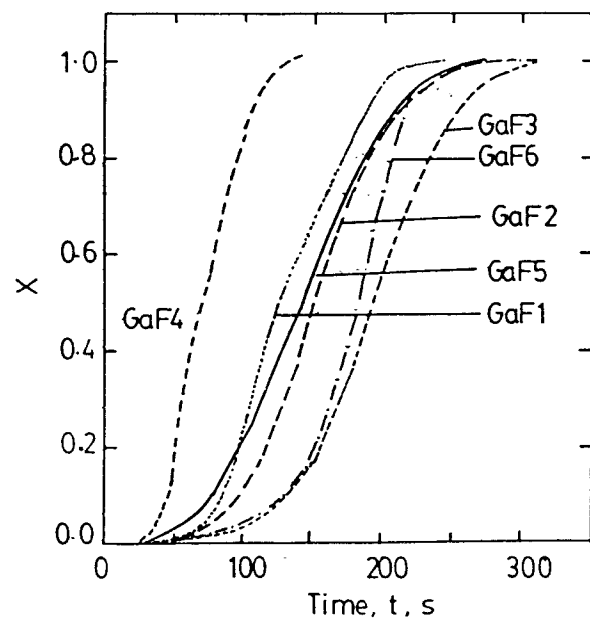Figure 1: Comparison of isochronal heating rate thermograms (20°C/min) for RAP glasses.

Figure 2: Comparison of the rate of phase transformation of the vitreous phase to crystals by plotting X vs t(s).

X-0.001

filled O:GaF3 3
open O: GaF1
open O:GaF1

open sq:GaF4

Temperature, °C

380
370
360
350
340

0.0 0.2 0.4 0.6 0.8 1.0

Time (seconds)

open traingle: GaF6
filled traingle: GaF5

X = 0.001

Temperature, °C

380
370
360
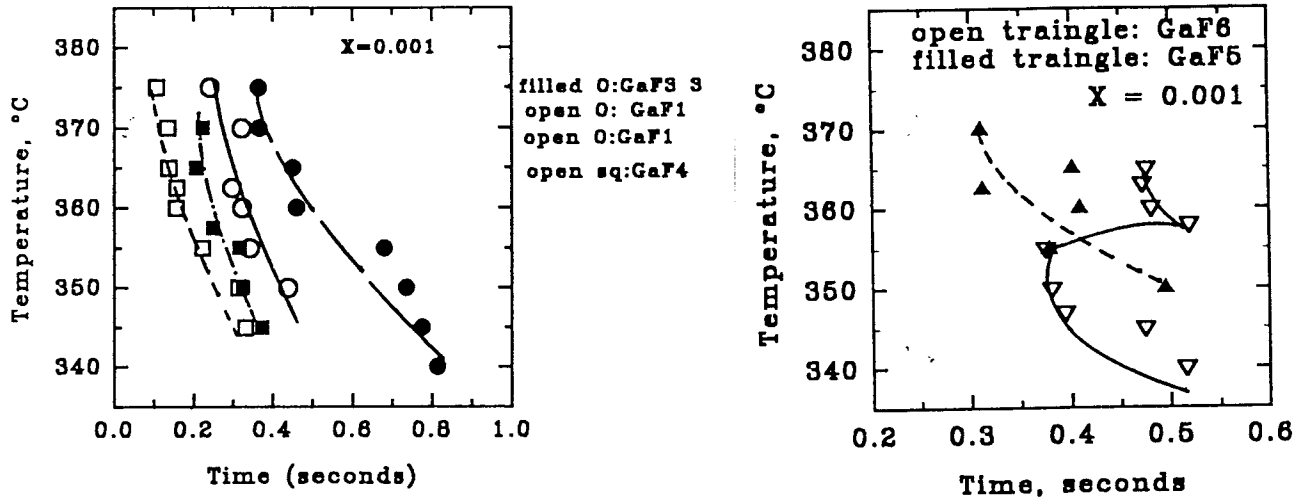350
340

0.2 0.3 0.4 0.5 0.6

Time, seconds

Figure 3: Plots of time-temperature-transformation (t-t-t) curves for RAP glasses.
(3a) t-t-t curves for GaF1 to GaF4 glasses. (3b) t-t-t curves for GaF5 and GaF6 glasses.

GaF4

GaF1

GaF6

10^2

10^1

10^0

loss, α, dB/m

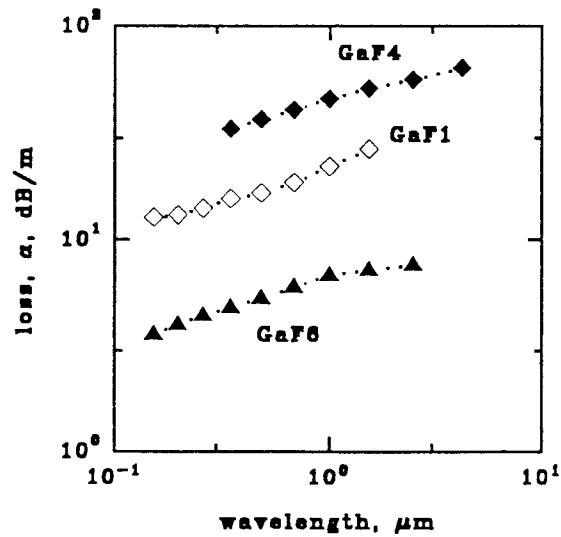10^{-1} 10^0 10^1

wavelength, μm

Figure 4: Measured multimode unclad fibre loss curves.
Glass rods prior to drawing were not thoroughly polished.