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VISCOSITY MEASUREMENT IN HALIDE MELTS

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Abstract

Viscosities of two kinds of halide melts were measured at temperatures near the glass transition and above the melting point. The melts and glasses investigated were two fluoroaluminate glasses, a cadmium mixed halide and a cadmium halide phosphate glasses, and a gallium-indium fluoride glass. The fluoroaluminate glasses were designed as core and cladding for a Nd-doped 1.3 μm fibre amplifier, while the cadmium halide and cadmium phosphate glasses, were designed as core and cladding for the Pr-doped 1.3 μm fibre amplifier. The gallium fluoride glass was also designed as host for the Pr-doped amplifier. The cadmium mixed halide glass exhibits a strong non-Newtonian behaviour contrasting with near-Newtonian fluoroaluminate melts. The implications of these results on fibre drawing and low-loss fibre fabrication are discussed. Viscosity data were fitted to models, and the appropriateness of the fits is discussed.

1. Introduction

In the last 20 years fluoride glasses have attracted a great amount of interest for numerous fibre optic applications. Their proposed uses include low-loss infrared fibres and as hosts for active devices, such as amplifiers and lasers[1]. However, great difficulties have been encountered in developing low-loss fabrication of exotic fluoride fibres. Successful drawing of low-defect, low-loss fluoride fibres depends upon glass stability, which is a function of melt viscosity and thermodynamic factors governing crystal nucleation. The viscosity of fluoride melts and glasses, unlike that of silica, is non-Arrhenian, and decreases much faster with increasing temperature. This promotes growth of microcrystallites during fibre-drawing and leads to scattering and high losses in the resulting fibres. In order to achieve low-loss fibres, it is vital to know the viscous behaviour of the glass, and to control the drawing parameters accordingly.

In the present work we investigate three types of fluoride glass. One is fluoroaluminate glass, of which two compositions are studied. These glasses were designed as core and cladding for a Nd-doped 1.3 μm fibre amplifier. The other glasses were designed for a Pr-doped 1.3 μm fibre amplifier. Two cadmium-based compositions were studied: a cadmium mixed halide, intended as Pr-doped core glass, and a cadmium halide-phosphate, intended as cladding. The last glass was a gallium-indium composition.

2. Experimental methods

The glass samples were prepared using methods reported elsewhere[2]. Care was exercised to obtain glass with low impurity levels, since impurities affect glass and melt behaviour.

Viscosities above the melting point were measured at the National Physics Laboratory (UK) using the torque method. In the present experiments, the melt was contained inside a molybdenum crucible and a molybdenum bob was suspended so as to be immersed in the melt. The bob was made to spin at a set rotational speed at each given isotherm, and the viscosity was calculated from the resulting torque. In a perfect Newtonian fluid the torque, and therefore the viscosity, is independent of the rotational speed of the bob. Prior to carrying out rheological measurements, a test was carried out on all melts to check crucible degradation and melt contamination. Insignificant degradation of crucible and bob was observed.

Viscosities near glass transition were determined by two different methods. The viscosity of cadmium fluorophosphate glass, reported elsewhere[2], was measured using a rheometric technique in a twisting bar configuration. The low temperature viscosities of the two fluoroaluminate compositions were measured using a thermo-mechanical method.

3. Results

3.1 Cadmium-based glasses

Figure 1 shows the high temperature viscosity curves of the cadmium-based glasses. It is seen that the pure halide glass is strongly non-Newtonian, and that viscosity decreases with increasing bob rotation. This behaviour is far less marked in the cadmium phosphate glass which is seen to have only a modest non-Newtonian component.

The strong dependence of viscosity on shear, which is inverse in character, reveals two properties of the cadmium halide glass melt. First, a polymerization process is taking place, its rate enhancing rapidly with increasing temperature. This is indicated by the sharp divergence of the two cadmium halide viscosity curves, for 30 and 60 rpm, in Figure 1. Second, the polymer bonds are weak in nature, as demonstrated by the fact that they can be broken by the drag force of the rotating bob.

The cadmium phosphate glass, by contrast, exhibits only a slight non-Newtonian behaviour. At the same time, a previous study[2] has shown that this glass contains phosphate polymer chains which determine many of its properties. The conclusion arises, therefore, that the phosphate bonds are strong enough to resist breaking under the force of bob rotation, and as a consequence this type of experiment results in shear-independent viscosity.

Figure 2 shows the viscous behaviour of the cadmium phosphate melt over the range of temperatures from glass transition to above melting; the viscosity at 60 rpm bob speed was used in the high-temperature region. The lines are fits to the Cohen-Grest and Eyring models. The behaviour is non-Arrhenian, as expected of a fluoride glass, but the gradual slope of the curve indicates that the glass is not particularly fragile. However, the slow change in viscosity

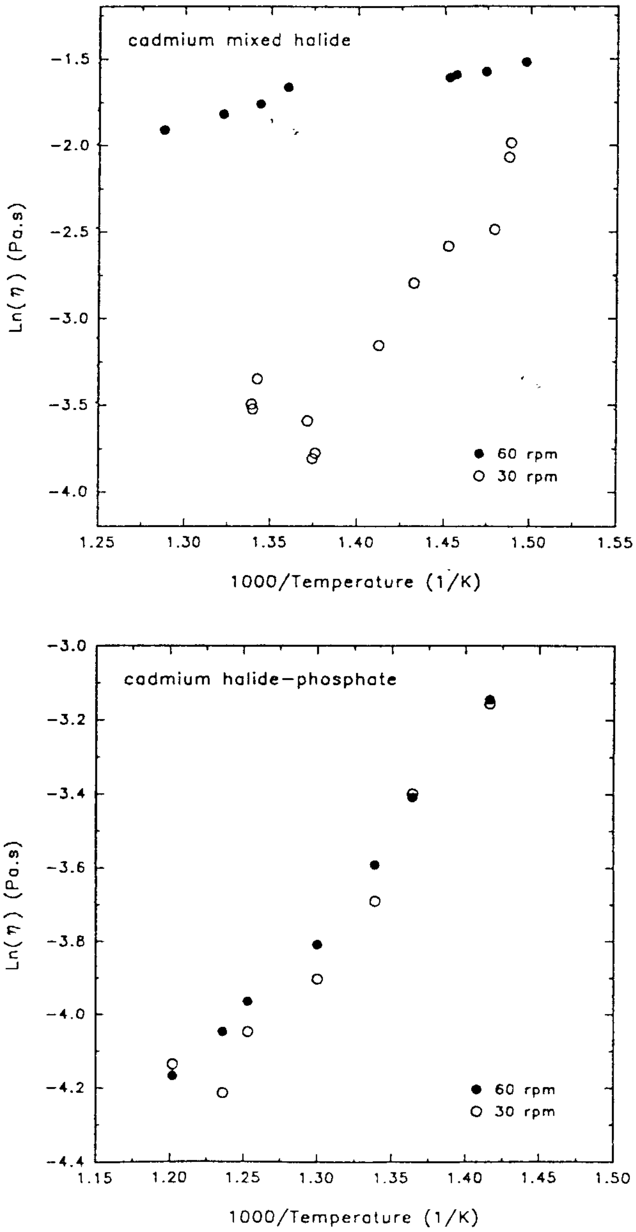

Figure 1. Viscous behaviour of cadmium-based glasses above melting point.

may be owed to the continuous bond-formation process of polymerization, which offsets the bond-breaking between structural units.

3.2 *Gallium fluoride glass*

Figure 3 shows the high-temperature viscous behaviour of the gallium fluoride glass melt. It is seen that the non-Newtonian characteristic is far less pronounced than in the cadmium halide melt. There is not enough evidence to estimate the degree of polymerization in the gallium fluoride glass. However, the reduced shear dependence of viscosity, as compared with the cadmium halide glass, is consistent with the fact that bond strengths are much higher in the gallium fluoride, as revealed by its higher characteristic temperatures and vibrational frequencies. E.g., the glass transition temperature and the dominant phonon peak of gallium fluoride glass are respectively 280°C and 500 cm^{-1}, compared with 120°C and 370 cm^{-1} in cadmium halide. The stronger bonds persist better under shear stress, and the effect on viscosity is much diminished.

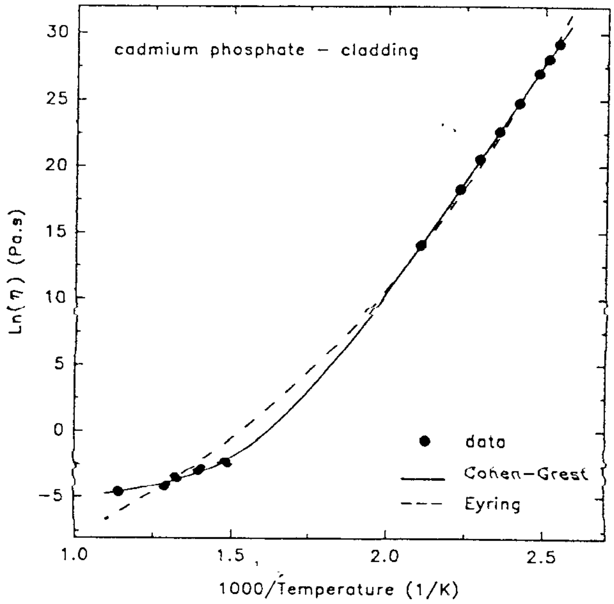

Figure 2. Viscosity curve of cadmium phosphate glass.

3.3 *Fluoroaluminate glasses*

Figure 4 shows the viscosity curves of the two fluoroaluminate glasses over the range of temperatures from glass transition to above melting point. The lines are fits to the Cohen-Grest and Eyring models. The two viscosity curves are very similar, confirming that the glasses are well matched as fibre core and cladding.

The abrupt slopes and sharp bends in the viscosity curves imply that these glasses are more fragile than the cadmium halide glass. Both glasses undergo a collapse of structure, after which the viscosity falls very rapidly with increasing temperature. However, from the point of view of fibre drawing, these glasses offer a relatively easy task, since their characteristic temperatures are relatively high (e.g. T_g=430°C) and the drawing takes place at temperatures below the low viscosity regime. The fragility of these glasses and the rapid change in viscosity indicate the absence of polymerization processes in the melt. As the bonds between structural units weaken and break at elevated temperatures, the viscosity drops abruptly.

Figure 5 shows the high-temperature viscosities of the two glasses for two rotational speeds of the bob. It is seen that both glasses are nearly Newtonian in their behaviour. This supports the view that there is no polymerization in these glasses.

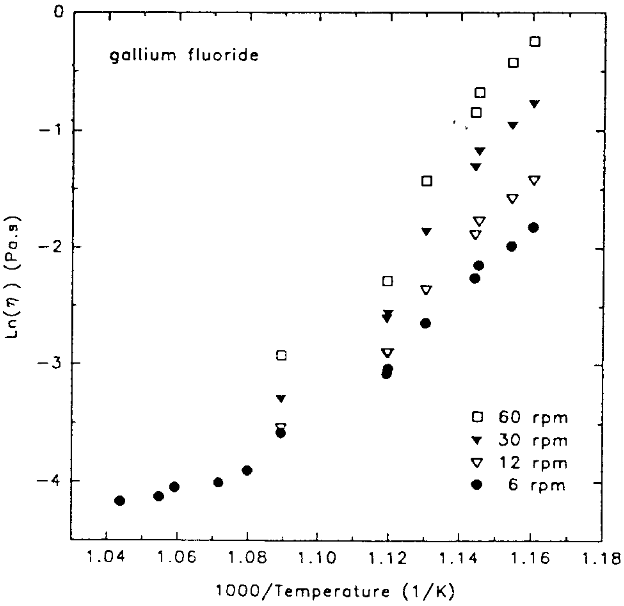

Figure 3. Viscous behaviour of gallium fluoride glass above melting point.

4. Discussion

The analysis of viscosity curves of the three glasses was based on previous work on fluoride glasses by Jha and Parker[3]. The viscosity curves in Figures 2 and 4 were fitted to two viscosity models, Cohen-Grest and Eyring. The fit parameters are listed in Table 1 below.

Both Cohen-Grest and Eyring models assume the Doolittle function for the shear viscosity, and use a varying free volume component. The Doolittle viscosity equation is an extension of the Arrhenius equation, modified to take into account the change with temperature of the free volume and the resulting effect on viscosity. It has the form[3]:

$$\eta = \eta_0 \exp(B/f_T) \qquad (1)$$

where η is the viscosity, η_0 and B are constants, and f_T is the free volume.

The Cohen-Grest model derives the free volume as having the form:

$$f_T = (T-T_0) + [(T-T_0)^2 + 4CT]^{1/2} \qquad (2)$$

where T_0 and C are adjustable parameters. T_0 can be interpreted as representing a transformation temperature, such as glass transition. The Cohen-Grest equation is usually capable of matching a good fit to a wide variety of viscosity data, as is seen here in Figures 2 and 4.

This is a direct consequence of its mathematical form, which incorporates both a quadratic and a square root functions. The fitting parameters can be adjusted to give a good fit to a very wide range of curves, provided that the curve in question has a first derivative that is everywhere positive and smoothly increasing. The goodness of the fit, however, derives from its mathematical form, and should not be interpreted as a true reflection of glass properties.

The Eyring model is based on the hole theory and assumes the free volume to be:

$$f_T = C\exp(-\Delta H/RT) \qquad (3)$$

where ΔH is the free energy of hole formation or activation enthalpy for shear viscosity, and C is a constant. Due to its exponential form, the curve of the Eyring model is "rigid", i.e. the curvature is close to constant over the usual experimental temperature range. The fit to data is therefore often poor, as is the case here. This is not surprising, given the complexity of these

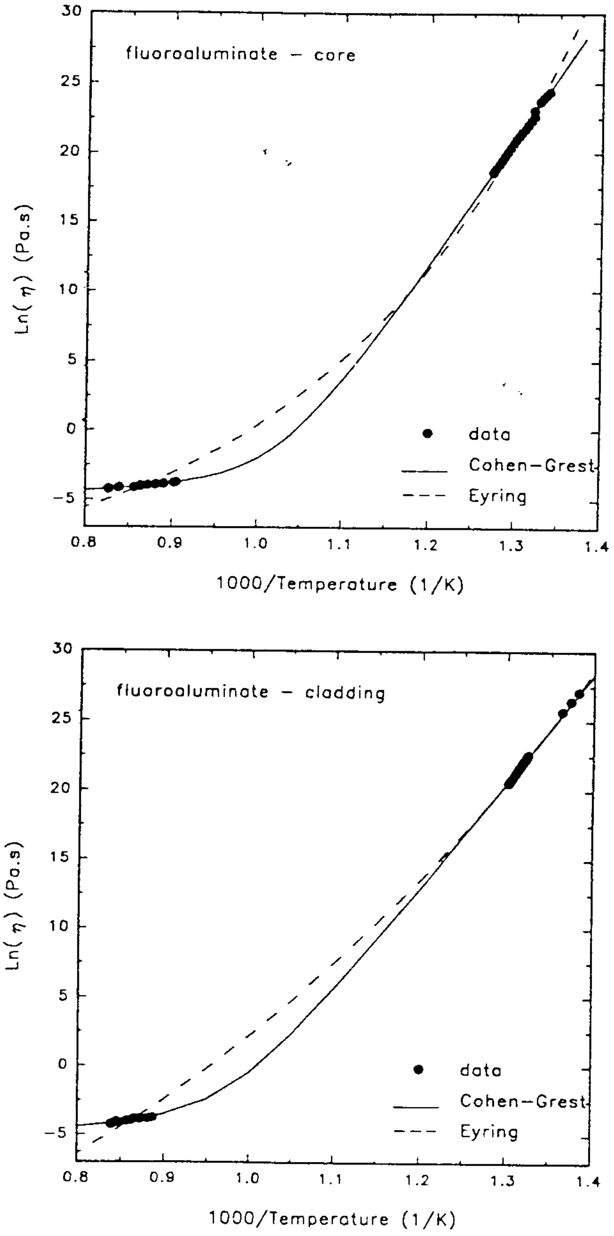

Figure 4. Viscosity curves of fluoroaluminate glasses.

glasses, and the multiplicity of types of structural units. The Eyring model assumes a single-valued activation enthalpy, based on a single type of structural unit. By contrast, all three glasses exhibit double and triple characteristic temperature peaks in non-isothermal scans, revealing their complex structure.

Moreover, the small non-Newtonian component of viscosity signals the presence of additional processes in the glass. These are not taken into account by glass viscosity models which completely disregard the formation and dissolution of polymer chains.

The non-Newtonian behaviour of the cadmium halide glass has important implications for fibre drawing. As drawing speed is increased, viscosity decreases, leading to unstable fibre drawing conditions and enhanced crystallization. For good fibre quality, it is therefore necessary to avoid imposing shear stress, and to draw this glass at low speed and under low tension.

The two fluoroaluminate glasses have very similar viscous behaviours, as seen in Figure 4. This confirms that they are well matched as core and cladding for producing good quality fibre. However, since these glasses are fragile in the higher temperature range, it is necessary to carefully control the drawing temperature to avoid slipping into the low-viscosity regime.

The relative fragilities of fluoroaluminate and cadmium phosphate glasses are demonstrated explicitly in Figure 6 which plots their viscosity curves as a function of T_g/T. The viscosity of fluoroaluminate glass changes much more abruptly. As pointed out above, this may be explained by the continuous polymerization in the cadmium phosphate glass which to some extent counteracts the reduction of structural bond strength.

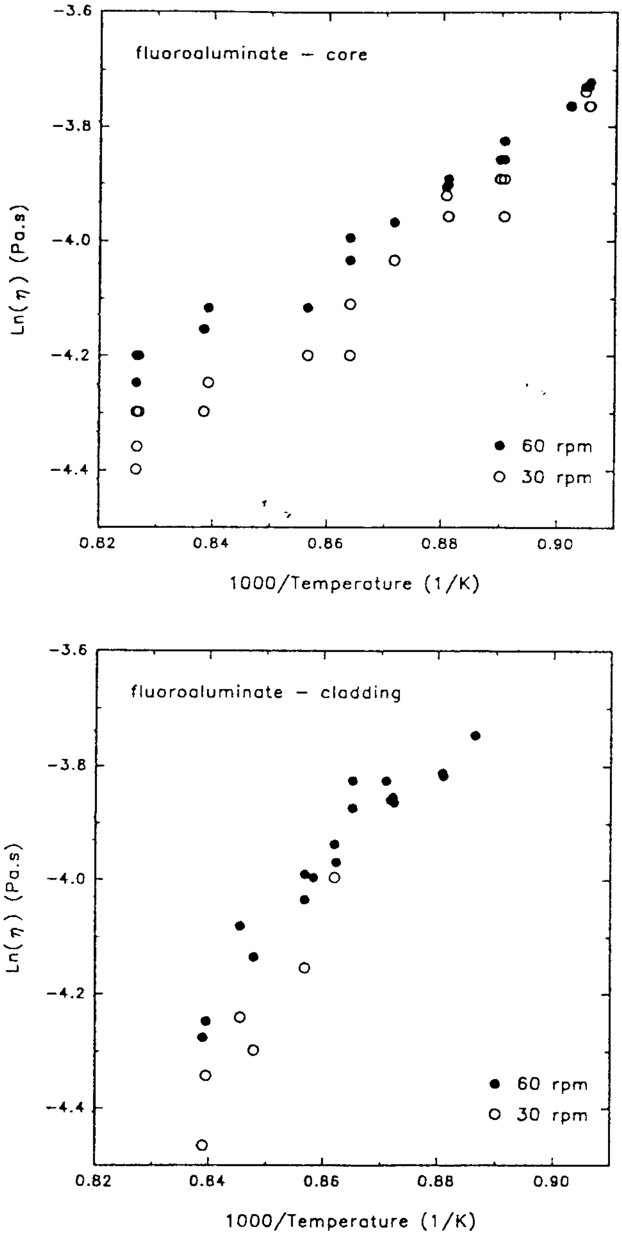

Figure 5. Viscous behaviour of fluoroaluminate glasses above melting.

5. Conclusions

The viscosities of cadmium halide-phosphate and two fluoroaluminate glasses were measured in the temperature range from around glass transition to above melting point. The viscosities of cadmium mixed halide and gallium fluoride were measured in the regime above the melting temperature.

The two fluoroaluminate glasses, designed as core and cladding for a fibre structure, were shown to be well matched and compatible. The steepness of the viscosity curve indicates that particular care must be taken to produce good quality fibre. The glasses exhibited nearly Newtonian behaviour, implying absence of polymer chains in the glass structure.

The cadmium halide-phosphate glass also demonstrated near Newtonian behaviour, combined with reduced fragility. This confirms that the glass is a good candidate for fibre drawing.

The cadmium mixed halide glass exhibited strongly non-Newtonian behaviour, with substantial decrease in viscosity with increasing shear. This indicates the presence of significant polymerization in the glass, which can be used to improve glass quality. Particular care must be exercised in drawing this glass to avoid imposing shear stress.

The gallium fluoride glass demonstrated modest non-Newtonian behaviour, intermediate between cadmium halide and fluoroaluminate glasses. This indicates the presence of considerable polymerization, and signals that fibre drawing must be carried out at low speed and under low tension.

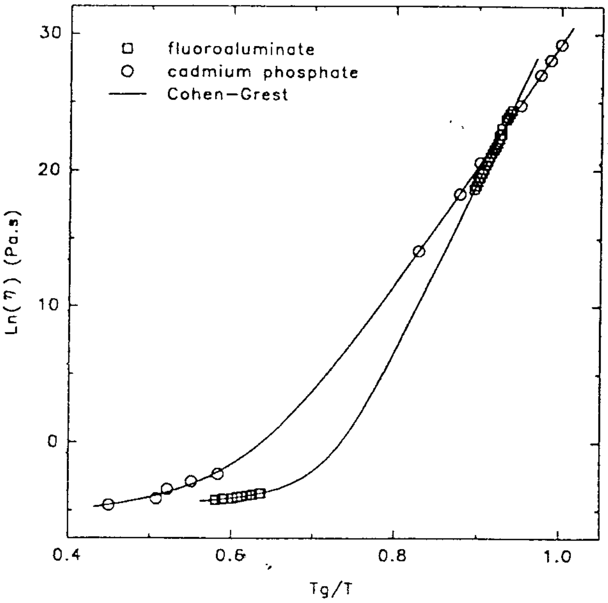

Figure 6. Comparison of cadmium phosphate and fluoroaluminate glasses.

Table 1: Fitting parameters for viscosity curves

Glass	Cohen-Grest	Eyring
fluoroaluminate - cladding	$\ln \eta_0 = -5.3$ (Pa.s) B = 430 K $T_0 = 1020$ K C = 2.8 K	$\ln \eta_0 = -33$ (Pa) B/C = 8.9 $\Delta H/R = 1390$ K
fluoroaluminate - core	$\ln \eta_0 = -4.9$ (Pa.s) B = 360 K $T_0 = 970$ K C = 1.9 K	$\ln \eta_0 = -12$ (Pa) B/C = 0.50 $\Delta H/R = 3220$ K
cadmium phosphate - cladding	$\ln \eta_0 = -6.0$ (Pa.s) B = 810 K $T_0 = 610$ K C = 6.7 K	$\ln \eta_0 = -22$ (Pa) B/C = 6.0 $\Delta H/R = 845$ K

References

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