MODIFYING BINARY Ga_2S_3 - La_2S_3 GLASS BY THE ADDITION OF A THIRD COMPONENT

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ABSTRACT

To further improve the workability of Ga_2S_3-La_2S_3 (GLS) glass for fibre fabrication, we have put a series of third components (both sulphides, i.e. Na_2S, CaS and In_2S_3, and halides, LaR_3, R = F, Cl, Br and I) into the binary GLS system. This paper describes the effect of various third components on the thermal, rheological and optical properties of the GLS. The structural role of each individual addition to the GLS glass was analysed upon its chemical bonding characteristics. Some modified GLS glasses show much enhanced UV transmission and greater workability for fibre fabrication.

1. INTRODUCTION

Using an erbium-doped fibre amplifier to directly amplify optical signals in the optical transmission systems has achieved unprecedented success since its discovery in 1986. The devices have already become commercially available since 1990 for long-haul tele-communication systems operating in the third low-loss window at a wavelength around 1.55 μm. However, most of the world's installed land-based fibre-optic networks are running at a wavelength close to 1.3 μm in the so-called second low-loss window of silica optical fibres used in the optical transmission systems. The erbium-doped amplifiers are not suitable for amplifying optical signals in the 1.3 μm region. Fibre amplifiers are, therefore, vigorously sought for transmission systems that amplify optical signals in the 1.3 μm wavelength region. Pr^{3+} and Dy^{3+} are the two rare-earth ions that have been proposed for use in 1.3 μm fibre amplifiers. Because the respective 1.3 μm fluorescent level in them has a rather narrow energy-gap relative to the next adjacent energy level, it becomes crucial that a low phonon-energy host material is used in order to minimize the nonradiative decay via multiphonon emission. The best performance reported so far has been the praseodymium doped fluoride fibre amplifiers (PDFFAs). Although fluoride (ZBLAN) host exhibits only about 4% quantum yield for the 1.3 μm emission, it has attained a small signal gain of around 23 dB with about 120 mW of pump power from a single stripe laser diode. In practice however, the high pump power required severely shortens the lifetime of the pump diode and consequently inhibits its commercial application.

In order to construct a more pump efficient Pr^{3+}- (or Dy^{3+}-) doped 1.3 μm fibre amplifier, it is therefore critical that the chosen host must have a maximum phonon energy notably lower than that (580 cm^{-1}) of the ZBLAN glass. Accordingly, it has been proposed to use chalcogenide glass as the host. It typically has a maximum phonon energy less than 450 cm^{-1}, which sufficiently reduces the probability for multiphonon emission and substantially increases the quantum yield and, subsequently, the pump efficiency for the device. Among the known chalcogenide glass forming compositions, the gallium lanthanum sulphide (GLS) glasses have been identified as one of the most promising candidates, mainly due to their good visible transmission and excellent rare-earth solubility.

Fibre fabrication from the gallium lanthanum sulfide (GLS) glasses has been demonstrated recently at our laboratories [1], but not without difficulties. The thermal stability of the GLS glasses at the temperature where the fibre drawing can be carried out is relatively low. This is chiefly because of the temperature of suitable viscosity for fibre drawing is just slightly lower than that of the onset of crystallization in these glasses. As a result, successful fibre drawing requires a great deal of dedication in keeping the fibre drawing furnace with a highly reliable temperature stability and accuracy. This in reality can be extremely difficult to fulfil. Therefore, modified GLS glass-forming systems are contemplated in order to attain glass compositions of improved thermal stability as to further assure avoidance of devitrification in fibre drawing and of enhanced optical transmission at the UV/Visible region for efficient pumping of active ions. This paper describes the effect of various third components on the thermal, rheological and optical properties of the GLS. The structural role of each individual addition in the GLS glass is analysed upon its chemical bonding characteristics.

2. EXPERIMENTALS

Fabrication of the modified GLS glasses is achieved by melting, then quenching, the designated batch mixture of suitable amount of high purity sulfides and halide through a multi-step temperature process in a vitreous carbon crucible inside a silica tube. The well-mixed powder batch is prepared in a nitrogen-purged glovebox before moving into the crucible placed in a silica tube. The multi-step temperature process is aimed at fully compounding the batch constituents to facilitate in assuring a structually homogeneous glass. One typical temperature process, for example, is to increase temperature slowly at 1°C/min first to 300°C for 5hrs, and at 2°C/min to 500°C for another 5hrs, then at 3°C/min to 650°C again for 5hrs and finally at 4°C/min to 1150°C for 3hrs for a batch of about 50 grams in weight. After quenching, the glass is transferred into an annealing furnace operating at about 450°C - 550°C, depending on the glass composition, for 6-12 hours.

Thermal properties of the modified GLS glasses are analysed by a differential thermal analysis (DTA) technique using a Perkin-Elmer DTA-7 thermal analyzer operating at a heating rate of 20°C/min. The thermal stability of a glass is commonly expressed either by the temperature difference between the onset of crystallization, T_x, and the glass transition, T_g, ie, $(T_x - T_g)$, or by the so-called Hruby factor, $H_r = (T_x - T_g)/(T_m - T_x)$, where T_m is the melting temperature. The greater is the $(T_x - T_g)$ or the H_r, the more stable the glass is. A typical differential thermal analysis curve for the GLS glass is presented in figure 1, together with the determinations for the characteristic temperatures T_g, T_x and T_m.

Viscosity of the glasses is measured using a parallel plate rheometry achieved by adapting a Perkin-Elmer TMA-7 thermo-mechanical analyzer [2], which operates up to 1000 °C and has a displacement sensitivity as high as 50 nm. The sample disc typically has a size of about 4 to 5 mm in both thickness and diameter. The parallel plates used are of high grade heat-resistant Inconel of 0.1 mm in thickness and 8 mm in diameter. The sample probe consists of a 100 mm long silica-rod with a perpendicularly placed silica-disc of 8 mm in diameter at its end. The silica sample cell, which has a sample platform of 10 mm in diameter, is purged with He gas during the measurement to ensure a rapid temperature equilibrium. The measurement is performed by firstly holding the sample disc, sandwiched between the parallel plates and under a fixed force, at T_g for 30 minutes in securing a structural equilibrium state in the sample. Then, the sample compression as a function of time (or temperature) is recorded by raising the temperature at a heating rate of 2 to 10 °C/min under a force of 100 to 2000 mN applied through the probe, depending upon the viscosity range of interest. Generally, the lower viscosity data are acquired by employing a faster heating rate and a smaller applied force, and higher viscosity data by a

slower heating rate and a stronger applied force. The recording is terminated once the diameter of the sample disc has approached that of the plates. Finally, the viscosity is calculated through the following equation[3]:

$$\eta = \frac{2\pi F h^5(t)}{3V [dh(t)/dt] [2\pi h^3(t) + V]} \quad (1)$$

where η is the viscosity (in poise), F is the applied force (in dyne), h(t) is the sample thickness at the time t (cm), dh(t)/dt is the compression rate at the time t (cm/sec) and V is the sample volume (cm^3). The procedure has been applied to the standard glass, NIST 710a, purchased from NIST (National Institute for Standard and Technology) for viscosity calibration at a variety of different conditions, by varying both the heating rate (2 to 10 °C/min) and the applied force (100 to 2000 mN). The results show excellent agreement with the standard viscosity data supplied by the NIST within ± 4 °C in the range of 10^{11} to 10^5 poise measured on the NIST 710a glass.

Optical transmission (or absorption) spectrum of the glass is measured by using a Perkin-Elmer Lambda 9 dual beam, double grating spectrometer in the UV/Visible region and a Perkin-Elmer Fourier transform infrared spectrometer (FTIR) in the infrared. Raman spectrum is taken on a triple grating micro-Raman spectrometer, pumped typically at a wavelength of 514.5 nm from an Ar ion laser.

3. RESULTS

3.1 Thermal Properties

Two types of compounds are introduced to the primary binary 70Ga2S3-30La2S3 glass as the third component, namely, sulfide and halide, in order to achieve the thermally more stable glasses. Among the sulfides, we have experimented with Na2S, CaS and In2S3. While the Na2S and CaS are added by substituting the La2S3, the In2S3 is introduced by replacing the Ga2S3 in the glass because of the closeness of the gallium and the indium in the Periodic Table. The systematic substitution of La2S3 by Na2S and CaS up to 15 mol% shows little improvement in the thermal properties. However, the similar substitution of Ga2S3 by In2S3 up to 30 mol% results in notable improvement in the glass thermal stability. Figure 1 presents the typical differential thermal ananlysis (DTA) curves with regard to the effect of addition of the third sulfide compound investigated on the thermal characteristic temperatures. As can been seen, the (Tx - Tg) gap remains virtually the same on the addition of Na2S

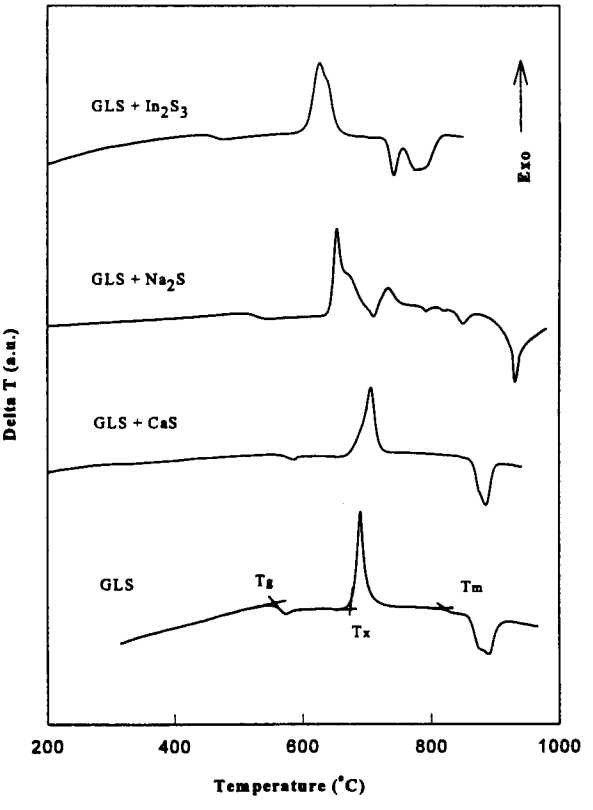

Fig.1. DTA plots showing effect of adding a third sulfide in GLS on the thermal properties.

and CaS, with Na_2S moving the gap slightly towards the lower temperature end and CaS shifting the gap to the higher temperature end. On the other hand, the substitution of Ga_2S_3 with In_2S_3 has resulted in a (T_x - T_g) gap as large as 160°C and the Hruby factor, Hr, of 1.6. This compares with the (T_x - T_g) gap of 120°C and Hruby factor of about 1.0 for the pure GLS glass.

Addition of a halide as the third component in the GLS is performed with the formula $70GaS_{1.5}(30\text{-}X)LaS_{1.5}XLaR_3$, R = F, Cl, Br and I. Figure 2 gives the effect of various halides on the stability parameter, (T_x - T_g), generated by using the DTA analyses. As can been seen, the addition of LaF_3 exhibits a constant deteriorating effect in the glasses, whereas $LaCl_3$ and $LaBr_3$ show improving effect on the thermal properties up to approximately 8 mol% with a peak around 2 to 3 mol%. The addition of LaI_3 into the GLS initially presents a decreasing effect up to 8 mol%, then it starts to show a strengthening effect on thermal stability with a peak around 20 mol%. The mechanism for the effect of each third component, either sulfide or halide, in the resulting GLS glass is discussed in section 4. Halide other than LaR_3, R = F, Cl, Br and I, as the third component in GLS is currently under investigation.

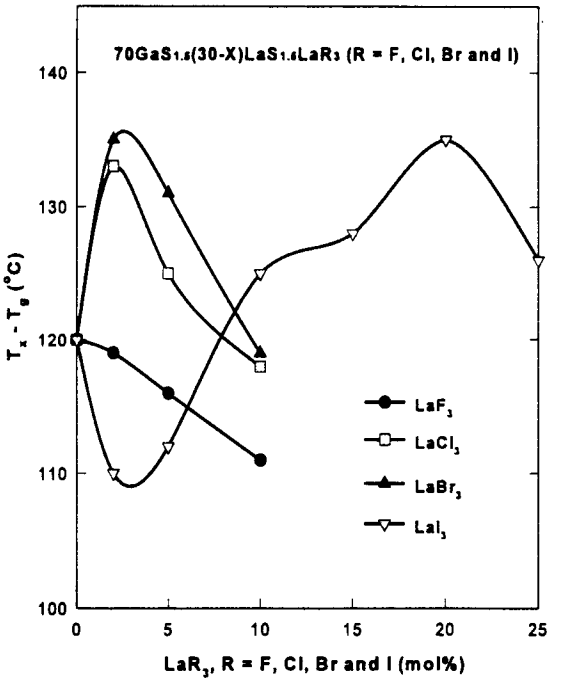

Fig. 2. Effect of various halide addition in GLS on the (T_x - T_g).

3.2 Viscosity

Examples of viscosities measured by using the parallel plate technique are presented in figure 3 for the GLS and a 20 mol% In_2S_3 modified GLS glass. The measurements are taken at a heating rate of 10°C/min and under an applied force of 200 mN. It is shown that the addition of In_2S_3 into the GLS rapidly reduces the melt viscosity by a decreased temperature in the order of around 100°C. However, the activation energy, E, for the viscous flow remains virtually the same with the In_2S_3 addition, as observed in the figure that the two curves show practically parallel with one another, at least, in the viscosity range measured.

It is generally adopted that the suitable viscosity, at which the fibre drawing can be conducted via the rod-in-tube method, is in the range of 10^6 -$10^{5.5}$ Poises [4]. By extrapolating the viscosity data into the range as shown in figure 3, it is found that the temperature for fibre

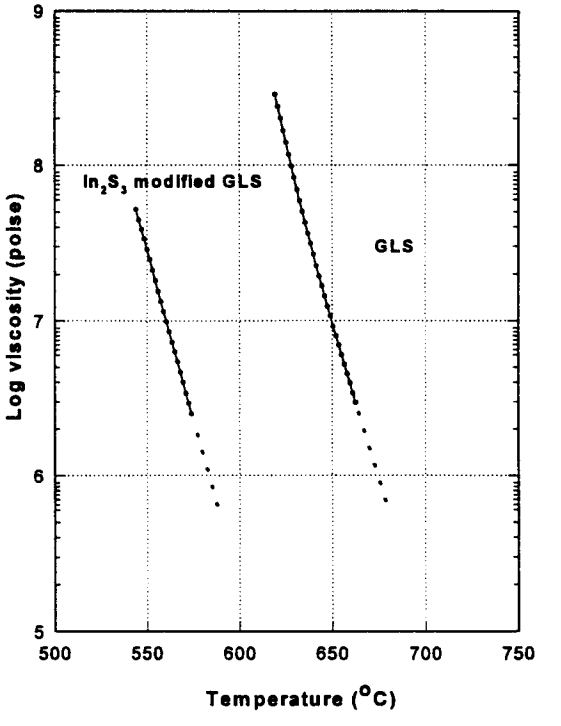

Fig.3. Viscosities of GLS and In_2S_3 modified GLS glasses

drawing for the In_2S_3 modified glass is around 580°C well below Tx (= 605°C), the onset for crystallization. Successful fibre drawing has been demonstrated from this glass. On the other hand, only a minor temperature difference is found for the pure GLS. However, fibre has also been realized from the GLS by using a fibre drawing technique, which to a certain extent suppresses the crystallization tendency, together with an effort in keeping the fibre drawing furnace with a highly reliable temperature stability and accuracy.

3.3 Optical Properties

Good UV/Visible transparency of the glass is of great importance in achieving efficient pump of active rare-earth ions doped into the glass used in optical devices. On the other hand, satisfactory transmission in the infrared region means low phonon-energy for the glass and, consequently, reduces considerably nonradiative multiphonon emission from the fluorescent level concerned of the rare-earth doped into the glass. It is found that the progressive addition of halide gradually improves the UV/Visible transmission in the glass, as the color of the glasses changes from the pale red in the pure GLS to the light greenish yellow in the heavily halide modified GLS. Among the sulfides, the color shows little change with the addition of Na_2S. Whereas the color becomes lighter with the addition of CaS and darker with the addition of In_2S_3. Figure 4 shows the representative examples of the UV/Visible transmission spectra of the various GLS glasses. However, addition of various third components into the GLS shows a little notable influence on the infrared transmission chracteristics as observed from the FTIR and Raman measurements. This indicates that the Ga_2S_3 is the dominant factor in these glasses with regard to the infrared transmission. While all components in the glasses contribute to influence the UV/Visible transmission property.

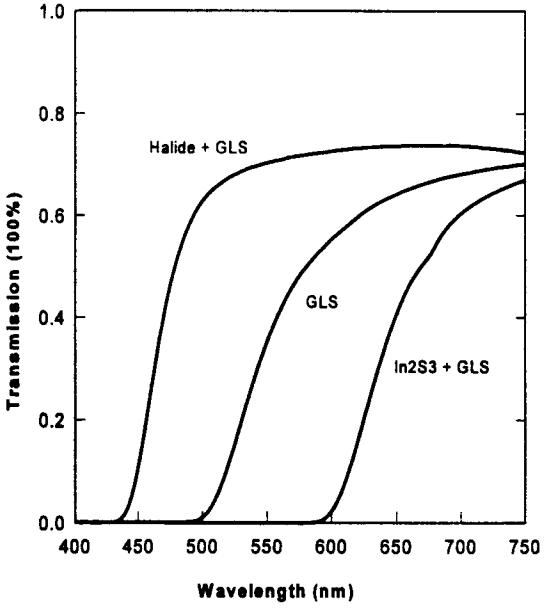

Fig.4 UV/Visible transmission spectra of various GLS glasses.

4. DISCUSSION

The structure of GLS glasses reported [5] consists of a covalent network of [GaS_4] tetrahedra, intercalated by the relatively ionic La - S channels, characterised by using an EXAFS (extended X-ray absorption fine structure) technique. This description is a close resemblance to the modified-random-network structural model proposed for the alkali silicate glasses [6]. However, it is in deep contrast to the structural rules generally followed by the conventional chalcogenide glasses. In conventional chalcogenide glasses, all chemical bonds are essentially covalent and the coordination number of each participating element complies with the so-called 8-N rule, wherein N is the group number of the element concerned in the Periodic Table. We have evaluated the spectral properties of the Pr^{3+} doped into the GLS glass using the well established Judd-Ofelt analysis procedure. Among the three Judd-Ofelt intensity parameters Ω_2, Ω_4 and Ω_6, it is well known that the parameter Ω_2 is directly proportional to the covalency of the chemical bond relating the rare-earth in the glass. It is found that the Ω_2 has a value of 7.3×10^{-20}

cm^2 for the Pr^{3+} in the GLS. This compares with $15.4x10^{-20}$ cm^2 and $4.95x10^{-20}$ cm^2 for the same ion in a chalcogenide glass based on GeS_2 [7] and in a typical oxide glass [8] respectively. The results suggest that the La - S bonds in GLS glass do appear to be rather ionic, assuming the praseodymium has similar structural sites as the lanthanum in the glass; thus agree with the conclusions made by Benazeth et al on the structure of GLS glasses. Since the structure of GLS glasses follows essentially the modified random-network structural model, the structural role of Na_2S and CaS substituted into the glass can be regarded as the glass modifiers like La_2S_3. Accordingly, they are unlikely to further improve the glass stability as observed. By contrast, the structural role of the In_2S_3 in the glass may be considered as an intermediate in the glass, because the indium has an electronegativity of 1.5 in between those of gallium (1.8) and lanthanum (1.1). Hence, the indium is highly possible to be involved with the glass-forming network and further strengthens the glass forming ability.

Due to the closeness in electronegativity and covalent size between the sulfur and the halogen (except F), the addition of halide may enhance the glass formation in such a way that the halogen enters the covalent network by forming a structural tetrahedra unit, for example $[GaS_3R]$, where R is I, Br or Cl. In the structure, apart from the natural covalent bond, an additional halogen covalent coordinate (dative) bond (Ga−R→Ga) is also formed to account for the sulfur inadequacy of Ga_2S_3 itself forming a tetrahedra so that an extended three dimensional covalent network is constructed. Whereas, the charge is compensated by the cation coming into the system as the halide. Such a mechanism has been shown in a Cs:Ga:S:Cl glass [9].

5. CONCLUSION

Modifying binary gallium lanthanum sulfide (GLS) glass has been carried out with a third component of both sulfide and halide. The effect of the third addition on thermal, rheological and optical properties of the glass is investigated. Structural models for the modified GLS glasses are also proposed. It is shown that it is possible to achieve modified GLS glasses of greater workability for fibre fabrication and/or of enhanced UV/visible transmission for optical applications.

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