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Fabrication of low-OH GeS_2 glasses and multimode fibres for mid-IR applications

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ABSTRACT

The fabrication properties of ternary and quaternary GeS_2-based chalcogenide glasses are discussed in view of the removal impurities and control of crystallization by controlling the starting composition, raw materials purification and fabrication steps. The two specific compositions discussed for glass and fibre fabrication are: GeS_2-Ga_2S_3-CsI and GeS_2-Ga_2S_3-CsI-SnS which were optimised for multimode fibre fabrication by investigating the thermal and viscosity properties. For chemical process control in food, pharmaceutical and petrochemical industry, optical fibre sensors operating above 200^{o}C in chemical process environment are required. For food and pharmaceutical it is also safer to use materials which are non-toxic. With these aims in mind we focussed on designing the glass structure by raising the T_g from 350^{o}C in ternary glass composition to 450^{o}C. By modifying the glass structure with the addition of SnS, the probability of near-T_g and sub-T_g structural relaxation in optical fibres, derived from quaternary compositions.

For the analysis of structural modification in glass, we have systematically carried out Raman spectroscopy using 514 and 633 nm sources. We report changes in the structure as a function of composition. The Raman spectroscopic analysis is also complemented by the IR reflection and transmission spectroscopy for a more comprehensive characterisation the vibrational structures. The glass compositions were also analysed for their devitrification and near T_g relaxation behaviour. On the basis of the devitrification characteristics we have also characterised the thermal stabilities of various compositions under thermal cyclic loading in the transformation region. The structural relaxation behaviour above T_g was also characterised by using a differential mechanical analyser by measuring the viscosity.

INTRODUCTION

Germanium disulphide (GeS_2) based glasses are modelled on the structure of $[SiO_4]^{4-}$ structure in silicates. The main structural building block is $[GeS_4]^{4-}$ tetrahedron unit which forms the 3D-random network. In such a structure, the cation-anion bond length (R,Å) due to Ge^{4+}(0.53Å)-S^{2-}(1.84Å) pair (2.37Å) is larger than that in $[SiO_4]^{4-}$(R=1.74Å). The glass formation ability and composition in GeS_2 system has been very well known, as an extended IR material. However, little is known about the glass-forming system for fibre fabrication and its transmission properties. The larger bond length and lower value of electronegativity of sulphur atoms than that for oxygen in $[SiO_4]^{4-}$ and heavier Ge and S atoms than Si and O, makes GeS_2 based glass an ideal material for engineering extended mid-IR fibres. The structural approach, discussed above, is consistent with the linear harmonic oscillator model equation 1 for calculating the fundamental frequency (υ_o) of molecular vibration and estimation of IR absorption edge. In equation 1:

$$\upsilon_o = \frac{1}{2\pi}.\sqrt{\frac{f}{\mu}} \qquad ..1;$$

f is the force constant between the cation-anion pair and $\mu = \frac{m_1.m_2}{m_1 + m_2}$ is the reduced mass of the linear harmonic oscillator. In the Ge-S system, the glass formation occurs between the GeS-GeS_2 and GeS_2-GeS_{2+x} composition range; the more S-chain dominated glass formation occurs in the latter composition range when excess of sulphur is present in the matrix [1]. Unlike silica and silicate glass, the glass formation in the GeS_2 compositions is strongly dependent on the cooling rate [2]. In the GeS_2-based glass-forming system, the structure limits the solubility of rare-earth ions which then compromises the use of such glass materials for laser and amplifier related applications. In this respect, in our previous work we had reported the structural modification by incorporating CsI as a modifier, so that the introducing large cations and anions of Cs^+ and I^- ions, respectively, opens the GeS_2 3D-network by creating more non-bridging sulphur sites at the corners of $[GeS_4]^{4-}$ structure. However, the incorporation of iodide then results in the increased S-S bonding in the structure which can be broken by adding either another network former e.g. Ga^{3+} by forming $[GaS_4]^{4-}$ or a modifier, for example, Sn^{2+}

by forming SnS type of bonds. The quaternary compositions based on GeS_2-Ga_2S_3-CsI-(Sb_2S_3 or SnS/SnS_2) were also designed and their properties were reported elsewhere [3].

GeS_2-based family of glasses demonstrate large optical nonlinearity (n_2=0.92x10^{-20} m^2W^{-1}) which make such Kerr media suitable for use in optical switching and related four-wave mixing devices, including supercontinuum generation, which was demonstrated in a waveguide geometry using a 1550 nm pulsed source [4,5]. The opportunity to access the mid-IR range using GeS_2-based glass optical fibres is quite tempting which might open much greater potential for using 2µm CW and mode-locked lasers [6], and the lasers based on Dy^{3+} [7] and Pr^{3+} [8] doped fluoride, fluoro-tellurite and chalcogenide glasses. By integrating a rare-earth ion doped laser device, for example, with a passive chalcogenide optical fibres and waveguides [9] and mid-IR detectors will aid the development of sensors and imaging system in mid-IR. Amongst the proposed emerging applications of fibres and waveguides, the structural stability against thermal and radiation induced damage is critical, which is known to occur in softer chalcogenide glasses based on arsenic, selenium, antimony and tellurium. The paper focusses on engineering of glass compositions for fibre fabrication, for which the experimental methodologies are described below.

METHODOLOGIES AND RESULTS

The compositions in molar percentage of sulphide chemicals selected for chalcogenide glass making are listed in Table 1. The method adopted for chalcogenide glass melting demands the need for maintaining vacuum for melting precursor chemicals in a cleaned, dried and baked silica glass ampoule. The wall thickness of silica glass ampoule must be able to minimize any risk of failure at elevated temperature due to the increasing pressure of sulphur, which can cause an explosion. This is evident from the rise in the vapour pressure of sulphur in Figure 1, which is compared with the vapour pressures of other elements and compounds. The raw materials, vacuum encapsulated inside a silica ampoule, was maintained in the constant temperature zone of the resistance heated furnace. In this graphical representation of the heating schedule for the chalcogenide glass samples, the heating rate for melting procedure was kept constant at 1°C per minute. The materials inside the silica ampoule were heated slowly up to 1050°C with holding steps, as shown in Figure 1, which correspond to the melting points of the raw materials. The partially melted raw material was then melted for 10 hours at 1050°C, before being cooled down slowly to 800°C for quenching.

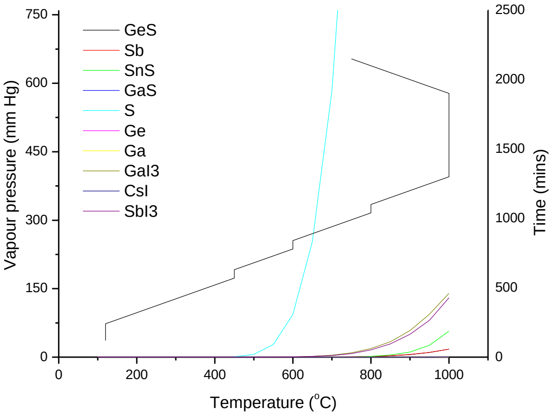

Figure 1: A general heating schedule for melting the CH family of glasses, listed in Table 1 below.

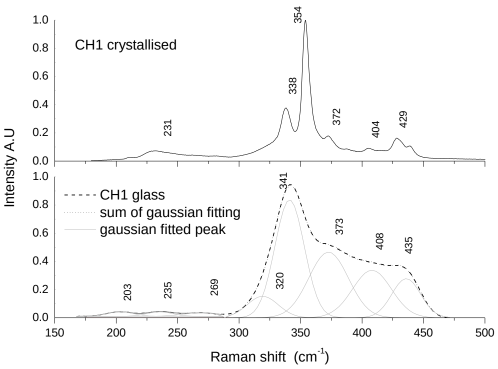

Figure 2: Raman spectra for glass CH1 (9GeS_2-15Ga_2S_3-6CsI) showing in the top graph the re-crystallised glass and in the lower graph the glass Raman spectra. $\lambda_{excitation}$= 514 nm.

Table 1: Compositions of GeS_2-based ternary and quaternary glasses designed for optical fibre fabrication studies and their characteristic temperatures (°C), determined by differential thermal analysis. The temperature differentials (T_x-T_g) and (T_m-T_x) are related with the stability parameters.

Glass ID	GeS_2	Ga_2S_3	CsI	SnS	Sb_2S_3	T_g	T_x	T_p	T_m	T_p-T_x	T_m-T_x
CH1	79	15	6	-	-	396	582	715	735	186	133
CH2	75	11	6	8	-	367	511	533	610	144	77
CH3	75	13	6	6	-	419	553	579	615	134	36
CH4	77	15	6	2	-	433	-	-	705	-	-
CH13	77	15	6	-	2	365	547	573	720	182	147
CH16	75	13	10	-	2	412	563	600	730	151	130
CH17	77	13	8	-	2	408	-	-	723	-	-

Note that the compositions CH4 and CH17 do not have discernible crystallisation, so that the T_x and T_p temperatures can be identified in the respective thermograms. The evidence for the lack of crystallization suggests that these two compositions are more thermally stable [10] than the others, reported in Table 1.

Figure 2 compares the Raman spectra of crystallised CH1 glass with its glassy state. The vibrational band structure for CH1 has been deconvoluted for identifying the contributing symmetric and anti-symmetric vibration modes, e.g. Ge-S in the GeS_4, Ga-S in GaS_4 and S-S in S_8 structures. Significant Raman bands observed were at 200 cm^{-1}, 235 cm^{-1}, 269cm^{-1}, 320 cm^{-1}, 341 cm^{-1}, 372 cm^{-1}, 408 cm^{-1} and 435 cm^{-1} wavenumbers, with lower wavenumbers below 300 cm^{-1} corresponding to the Ge-S-I type vibrations, attributed to GeI_2S_2 and GeI_3S structures [3]. In Figure 3, the bulk glass IR spectra are compared, with significant reduction in OH^- and corresponding Ge-O vibrations at around 3300cm^{-1} and 1250cm^{-1}, respectively in CH4 and CH17 glass samples. In these two compositions, the S-H and CO_2 absorption bands were also found to be much reduced due to the way the glass was processed.

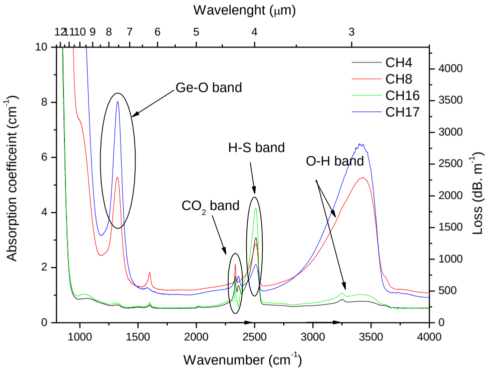

Figure 3: A comparison of FTIR data for selected chalcogenide glasses, shown in Table 1.

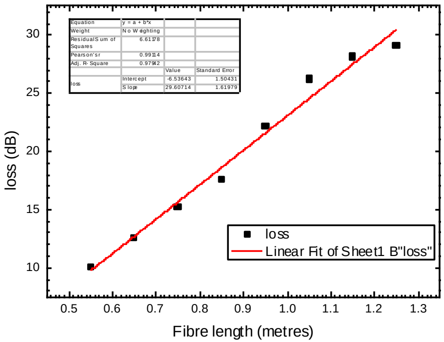

Figure 4: Loss characteristics of unclad CH4 glass fibres with ~125 μm average diameter.

The refractive indices of two thermally stable glasses (CH4 and CH17) were measured at 1550nm and were found to be 2.107 and 2.079, respectively. The coefficient of thermal expansion for these two glasses were $1.28x10^{-5}$ and $1.41x10^{-5}$ /°C, and the iso-viscosity points, $\log_{10}\eta=5$, PaS were at ~445°C and ~553°C, respectively. Based on the thermal, optical and spectroscopic data, a glass composition was first purified by drying the raw materials in vacuum in a baked silica ampoule which helped in removing OH^- impurities and had a dramatic influence in reducing the background loss, characterized in Figure 3.

CONCLUSIONS

Using the thermal and viscosity data of the CH4 glass, an unclad preform was made which was then drawn into unclad fibres. The loss properties of unclad fibre was measured and is shown in Figure 4, from which, as expected, the value of slope yields 29.1 dB/m loss high due to the presence of air cladding. During drawing the viscosity was maintained by controlling the temperature around 445°C. Although is the very first attempt for drawing such fibres with sulphur and iodine content and the results reported are for unclad fibres, the investigation provides a right direction for developing the core-clad structure fibres for potential mid-IR applications.

REFERENCES

[1] P. N. Kumta and S.H. Risbud, J Materials Science, **29**, 1135-1158 (1994).

[2] D Marchese, G Kakarantzas, A Jha, J Non-crystalline solids **196**, 314-319 (1996).

[3] CJ Hill and A Jha, J Non-crystalline solids **353** (13), 1372-1376 (2007).

[4] KS Bindra, HT Bookey, AK Kar, BS Wherrett, X Liu and A Jha: Appl. Phys. Lett. **79**, 1939 (2001).

[5] N D Psaila et al: Optics Express,. **15**, Issue 24,pp. 15776-15781 (2007).

[6] F Fusari, AA Lagatsky, B Richards, A Jha, W Sibbett, CTA Brown, Optics express **16** (23), 19146-19151 (2008).

[7] B Richards, TT Fernandez, G Jose, D Binks, A Jha, Laser Phy. Letters **10** (8), 085802 (2013).

[8] Z Tang et al: Optics Mat Express, **5**, Issue 4, pp. 870-886, (2015).

[9] A Ródenas et al: Optics Letters, 37, Issue 3, pp. 392-394, (2012).

[10] A Jha, Inorganic Glasses for Photonics, Chaps 1 & 2. John Wiley (2016).

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