1348

JOURNAL OF MODERN OPTICS, 1996, VOL. 43, NO. 5, 963–970

Spectroscopic and thermal properties of GeS_2-based chalcohalide glasses

D. MARCHESE, G. KAKARANTZAS, A. JHA
Department of Materials Technology, Brunel University,
Uxbridge UB8 3PH, England

B. N. SAMSON and J. WANG
Optoelectronics Research Centre, University of Southampton,
Southampton SO17 1BJ, England

(*Received 2 October 1995*)

Abstract. The low phonon energy of germanium sulphide glasses makes them ideal candidates as hosts for 1·3 μm fibre amplifier applications. However, the GeS_2 glass host suffers from a major drawback of poor rare-earth ion solubility. In an efficient device, the solubility of Pr ions has to be enhanced, without adversely affecting either the thermal or the spectroscopic properties of the glass. In the present investigation, we report the synthesis and optical properties of modified GeS_2-based chalcohalide glasses with excellent thermal characteristics suitable for drawing low-loss optical fibres.

1. Introduction

Chalcogenide glasses have been used as passive optical component materials since the early 1960s owing to their high transparency in the far infrared (IR). In the past few years, major advances have been made in the area of optical communications. The existing network requires upgrading with all optical devices. Sulphide-based chalcogenide glasses doped with Pr^{3+} are among the best candidates for fibre amplifiers in the second telecommunications window for two main reasons. Firstly, the low phonon energy of the host reduces the multiphonon relaxation from the $^1G_4$, which is the upper level of the $^1G_4$–$^3H_5$ stimulated transition at 1·3 μm (figure 1), thus increasing the gain coefficient; secondly, because of the high refractive index of the glasses (2·1–2·5), a larger stimulated cross-section is expected. Over the past few years, one of the most investigated sulphide hosts is the Ga–La–S (GLS) glass system [1–3] with low phonon energy (425 cm^{-1}) and high rare-earth solubility due to the presence of La ions. The major problem with GLS glass has been its poor thermal stability that has eluded the development of reasonably low-loss single-mode fibres. At the same time, the search for other potentially low-phonon-energy sulphide hosts has led to the GeS_2–Ga_2S_3 glass system [4–8] and As_2S_3 [7, 9]. The major drawback of the GeS_2 and As_2S_3 glass host is their poor rare-earth ion solubility compared with GLS glasses. The main advantage of GeS_2 and As_2S_3 systems over GLS is that both glass hosts are known to yield reasonably low-loss fibres. However, for designing an efficient and high-gain second-window fibre amplifier, the problems associated with poor rare-earth ion solubility in the GeS_2-based glass host has to be minimized without sacrificing their fibre-drawing characteristics. The improvement in fibre drawing is

0950-0340/96 $12·00

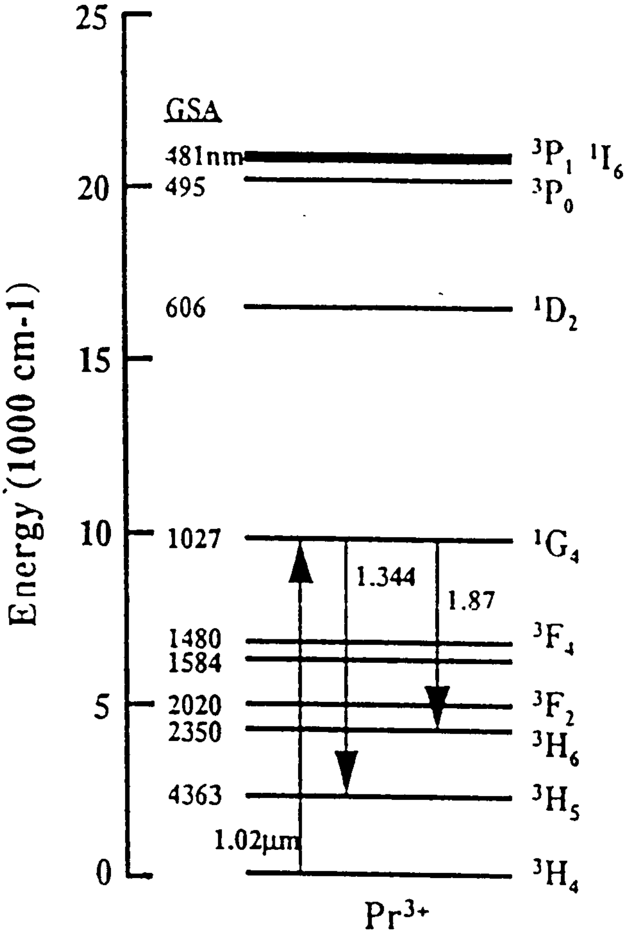

Figure 1. Energy level diagram of Pr^{3+}.

only possible by reducing the devitrification tendency of the glass host. This investigation discusses the improvement in spectroscopic and thermal properties of GeS_2-based glasses for Pr-doped second-window fibre amplifier.

2. Experimental details

For the glass preparation, germanium disulphide (GeS_2) powder from Merck of purity 99·99% was weighed and mixed with Ga_2S_3 (Merck) of the same purity inside a glove-box under a N_2 atmosphere. The modified germanium sulphide glass compositions contained a compound in the form of M_bX_c where M refers to either an alkali (Li, Na, K or Cs) or an alkaline earth (Ca, Sr or Ba) metal and X refers to a halogen (F, Cl, Br or I). The samples for spectroscopic characterization were doped with 2000 ppm of Pr_2S_3. Typical batch sizes were 10–15 g. The powder mixture was loaded into a silica glass ampoule and thoroughly dried using ultra-high vacuum to expel absorbed moisture. After drying, the silica ampoule was sealed off under high vacuum (10^{-6}) with an oxypropane flame. The sealed ampoules were slowly heated to 1050°C inside a vertical furnace and were kept at this temperature for 20 h for homogenization. After melting, the ampoule was removed and air cooled for a few minutes followed by annealing at the glass transition temperature for a period of 6 h. The annealed glass sample, which was roughly 15 mm in diameter and 15 mm in length, was cut and polished for optical and spectroscopic characterization.

The characteristic glass temperatures T_g and T_x were determined using a Perkin-Elmer differential thermal analysis (DTA) system at a heating rate of 20 K min^{-1}. A Nicolet SX Fourier transform IR spectrophotometer was used to determine the far-IR transparency of the glass. The ultraviolet (UV) cut-off wavelength and the characteristic Pr absorption lines were determined using a Perkin-Elmer Lambda 19 UV-visible-near-IR double-beam spectrophotometer. Fluorescence was measured on bulk samples using an Ar-ion-pumped Ti-sapphire tunable laser operating at 1020 nm as pump source and the emitted light was collected using a Ge detector. Lock-in techniques were used to improve the signal-to-noise ratio. The fluorescence lifetime could be determined by chopping the signal and detecting the decay of the fluorescence intensity on an oscilloscope. Finally the linear refractive indices of the samples were measured at 633 nm using the prism coupling technique.

3. Results and discussion

3.1. *Glass formation and thermal stability*

The compositions of binary chalcogenide glasses contained from 0 to 20 mol% Ga_2S_3 ($100 - xGeS_2$, xGa_2S_3). The compositions of the ternary glasses were the derivatives of binary compositions in which GeS_2 and Ga_2S_3 were replaced by the modifier M_bX_c leading finally to the composition domain $(100 - x)GeS_2$, $(20 - y)Ga_2S_3$, $(x + y)M_bX_c$. The binary and ternary compositions are designated by the symbols GSB.. and GST.. respectively. The thermal stability of the glass markedly improves with the addition of the halide-based modifiers. In most of the compositions, good-quality glass (10^{-4} fraction of crystals) could be obtained with just furnace cooling (at about 2 K min^{-1}). The thermal analysis data in the table indicate wide $T_x - T_g$ and $T_p - T_x$ gaps, where T_g, T_x and T_p are the onset temperatures for glass transition, crystallization and the peak of crystallization respectively. In some of the ternary compositions the $T_x - T_g$ can be as large as 228°C which is significantly higher than the largest gap for the binary compositions. This dramatic improvement in the thermal properties of the modified compositions together with the extremely low tendency towards devitrification makes fibre drawing in this glass system very feasible.

Thermal analysis data.

Glass number	T_g (°C)	T_x (°C)	T_p (°C)	$T_x - T_g$ (°C)
GSB1	487	639	657	152
GSB2	459	619	642	160
GST4	412	640	663	228
GST5	422	624	661	202
GST8	415	605	627	190
GST11	433	615	701	182
GST14	421	615	703	194
GST19	393	540	687	168

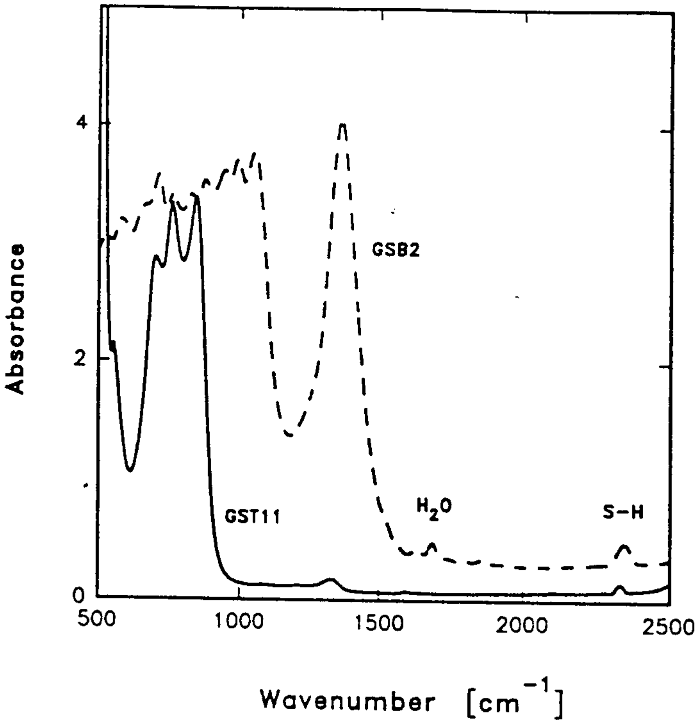

Figure 2. Far-IR absorbance spectra of GSB2 and GST11 glass samples.

3.2. *Transparency of the glasses*

In figure 2 the far-IR absorbance spectra of a binary and ternary glass are shown. It can be seen that there are several absorption peaks due to impurities such as H, O and moisture. Although the presence of halogen has a small contribution to the IR transparency, the IR cut-off edge is mainly dominated by the multiphonon process of Ge–S bonds [10]. Better processing during the glass preparation together with the use of higher-quality starting materials can result in a significant improvement in IR transparency, as shown in figure 2. The V-shaped curve for the intrinsic loss of characteristic glass composition is shown in figure 3. The intrinsic loss curve was determined using the fitted data for the loss due to Rayleigh scattering and due to the multiphonon processes. The minimum intrinsic loss is $\alpha_T = 1{\cdot}5 \times 10^{-2}$ dB km^{-1} at $\lambda_{\text{min}} = 5{\cdot}5$ µm. The loss at 1·3 µm is about 3·0 dB km^{-1}. The UV edges of a binary and ternary glass are shown in figure 4. The red shift of the ternary composition is probably due to the higher refractive index of the glass.

3.3. *Spectroscopy of Pr^{3+}-doped samples*

One of the main problems of chalcogenide hosts (except in the case of GLS) glass is the solubility of Pr ions. The close-packed network of GeS_2 (very similar case with fused silica) inhibits the incorporation of the rare earths. There is an improvement in the solubility of Pr ions with the addition of Ga_2S_3. In the present investigation the addition of M_bX_c modifiers has been found to enhance even more the solubility of Pr. Figure 5 shows the absorption spectrum of a ternary glass

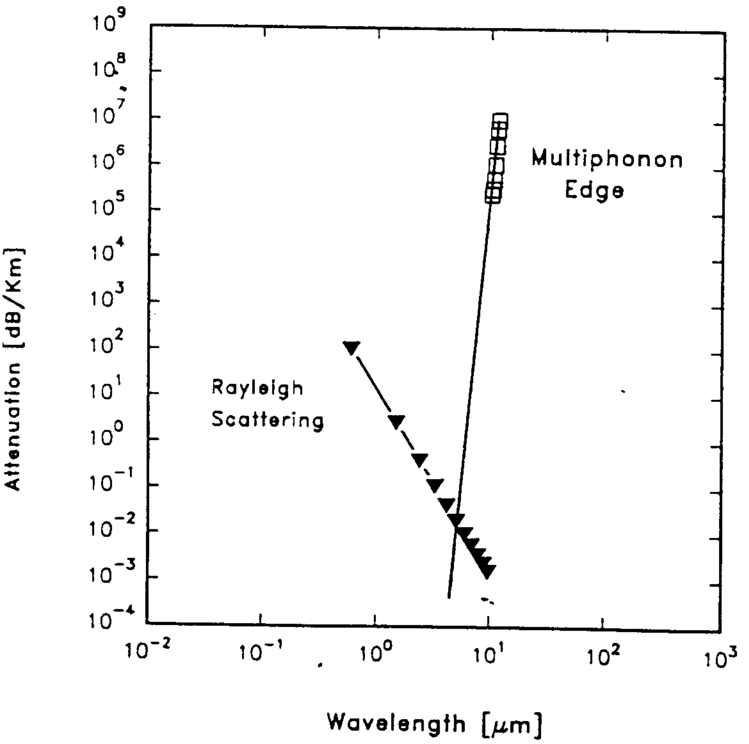

Figure 3. Intrinsic loss of GST11 glass due to Rayleigh scattering and multiphonon relaxation.

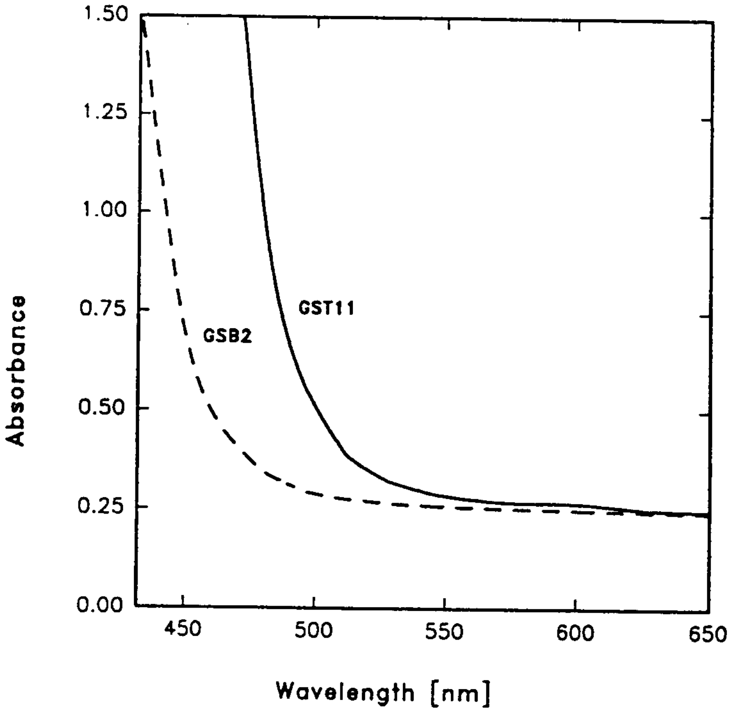

Figure 4. Absorption spectra for the UV electronic edge of the glasses GSB2 and GST11.

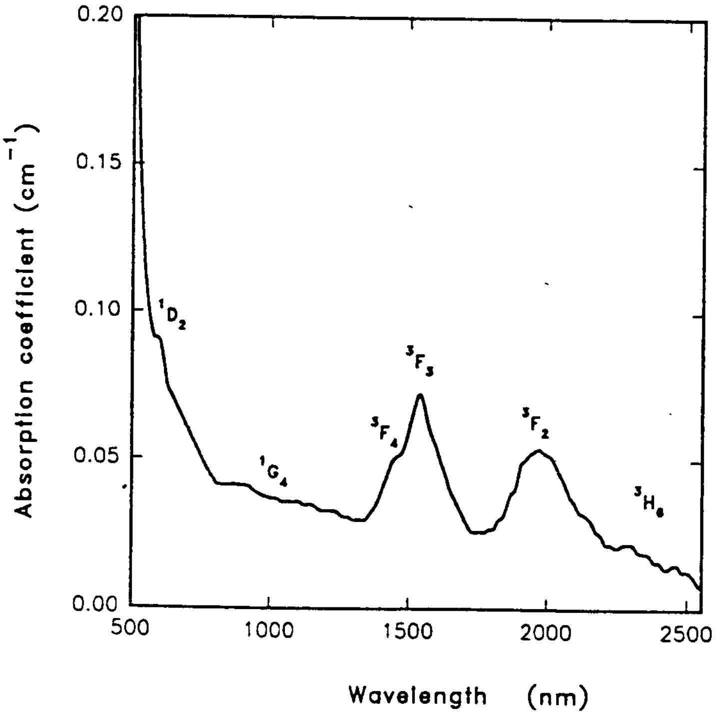

Figure 5. Absorption spectrum for Pr^{3+} in the GST11 chalcohalide glass.

sample doped with 2000 ppm Pr^{3+}. Absorption to six *J* levels of Pr_{3+} is observed in the region 500–2500 nm on this sample 2 mm thick. The emission band of the $^1G_4$–$^3H_5$ transition pumped at 1020 nm of the same ternary glass is shown in figure 6. The peak wavelength is at 1350 nm. A second small feature at 1290 nm can also be seen in the fluorescence spectrum and resembles the features seen in oxide-containing GLS glass samples. However, a more detailed study of any site selectivity is needed to verify its presence. The fluorescence lifetime varies from sample to sample. In samples with no impurity content the emission lifetime is reduced only by multiphonon relaxation, and the photoluminescence decay curve is of a single-exponential nature. In this study, the lifetimes were found to be non-exponential, which is probably related to some impurity content (OH or oxide) of the glasses and the high doping level (2000 ppm) of Pr. The lifetime of the best sample (fluorescence spectrum of figure 6) has a fast lifetime component (non-exponential behaviour) of about 120 μs over the first two e-folding times. Taking into account the high doping level (2000 ppm), this result is comparable with the results obtained by other workers [5, 7] for similar doping levels.

3.4. *Nonlinear properties*

Preliminary experiments suggest that the third-order nonlinearity is very high, especially for the compositions modified with M_bX_c. The improvement in the figures of merit representing the suitability of the material for switching applications can be ten times higher than those for the binary and unary compositions.

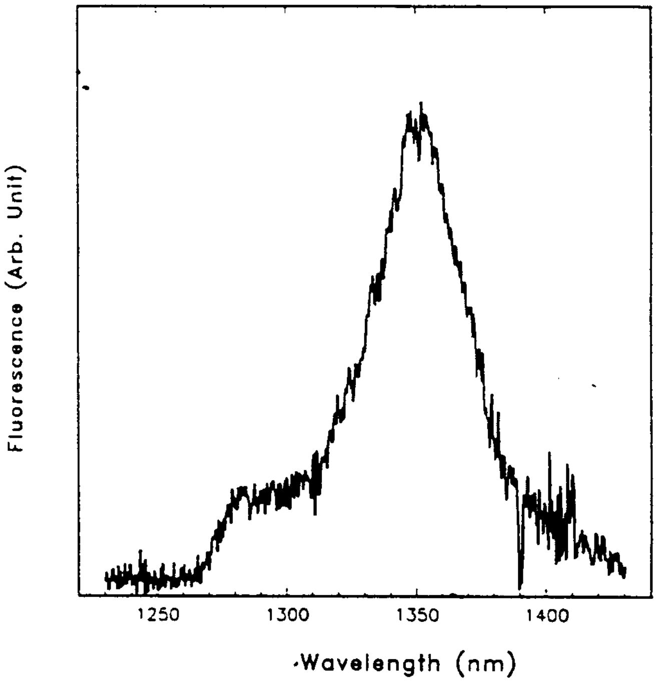

Figure 6. Fluorescence spectrum of Pr^{3+} in the GST11 glass.

4. Conclusions

GeS_2-based chalcogenide and chalcogenide glasses were successfully prepared with very high optical and thermal quality. The evidence for a wide $T_x - T_g$ gap of the modified ternary glass compositions makes them suitable candidates for fibre drawing. With a subsequent reduction of the doping level for Pr (less than 500 ppm) and the level of the impurity content, the modified ternary compositions are very promising candidate materials for 1·3 μm fibre amplifier applications.

Acknowledgments

The authors acknowledge financial support from the European Union in Brussels. Also, the authors gratefully acknowledge the technical assistance provided by Dr A. K. Kar from the Physics Department of Heriot–Watt University, and Dr D. W. Hewak of the Optoelectronics Research Centre at the University of Southampton.

References

[1] Becker, P. C., Broer, M. M., Lembrecht, V. G., Bruce, A. J., and Nycolak, G., 1992, *Proceedings of the OOA*, Sante Fe, 1992, Postdeadline Paper PD5 Optical Soc. America, pp. 20–23.

[2] Hewak, D. W., Hewak, D. W., Deol, R. S., Wang, J., Wylangowski, G., Neto, J. A. M., Samson, B. N., Laming, R. I., Brocklesby, W. S., Payne, D. N., Jha, A., Poulain, M., Olero, S., Surinach, S., and Baro, M. D., 1993. *Electron. Lett.*, 28, 238.

[3] Hewak, D. W., Madeiros Neto, J. A., Samson, B., Brown, R. S., Jedzejewski, K. P., Wang, J., Taylor, E., Laming, R. I., Wylangowski, G., and Payne, D. N., 1994, *IEEE Photon. Technol. Lett.*, 6, 609.

[4] Jha, A., Sapp, P., and Kakarantzas, G., 1995, *Proceedings of the Eighth World Congress on High Technology Ceramics, Topical Symposium*, Florence, 1994, Presentation SVII-7:LO4, *J. Adv. Sci. Technol.*, **11**, 391.
[5] Wei, K., Machewirth, D. P., Wenzel, J., Snitzer, E., and Sigel, G. H. Jr, 1994, *J. non-crystalline Solids*, **182**, 257.
[6] Simons, D. R., Faber, A. J., and de Waal, H., 1995, *Optics Lett.*, **20**, 468.
[7] Ohishi, Y., Mori, A., Kanamori, T., Fujiura, K., and Sudo, S., 1994, *Appl. Phys. Lett.*, **65**, 13.
[8] Simons, D. R., Faber, A. J., and de Waal, H., 1995, *J. non-crystalline Solids*, **185**, 283.
[9] Wei, K., Wenzel, J., Snitzer, E., and Sigel, G. H. Jr, 1993, *Fundamentals of Glass Science and Technology 1993*, Proceedings of the Second European Society of Glass Science and Technology Conference, Venice, 1993 (Venice: Statione Sperimetale del Vetro), p. 307.
[10] Heo, J., and Mackenzie, J. D., 1989, *J. non-crystalline Solids*, **111**, 29.