Transition metal-doped chalcogenide glasses for broadband near-infrared sources

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Abstract

In this paper we report the spectroscopic data for samples of 0.031% iron, 0.017% nickel, 0.01% chromium and 0.017% cobalt (molar) doped gallium lanthanum sulphide (GLS) glass. Photoluminescence (PL) with a full width half maximum (FWHM) of around 500 nm and peaking between 1120 nm and 1460 nm is observed when excited using wavelengths of 850 nm and 1064 nm. The emission lifetime for nickel-doped GLS at 300 K was measured to be 40 μ s. Photoluminescence excitation (PLE) peaks for chromium-doped GLS at 700 nm and 1020 nm have been observed. By comparisons of our spectroscopic data to that of transition metals doped into other hosts we determine the oxidation states of the transition metal ions and propose transitions for the observed spectroscopic peaks.

1. Introduction

Over the past few decades silica optical fibre has revolutionised the way in which we communicate, allowing low cost, high-bandwidth transmission of data over long distances hence enabling millions of people around the world access to data resources like the World Wide Web. Although silica's exceptional low loss of <1 dB/km at 1.55 μ m¹ makes it by far the best material for long distance communication, its low refractive index and inability to transmit radiation past 2 μ m make it unsuitable for many active and mid infrared (MIR) optical devices².

A key component of telecommunications networks, the erbium-doped fibre amplifier (EDFA) is the most widely used optical amplifier and has allowed transmission of large data volumes using a number of channels at different wavelengths through dense wavelength division multiplexing (DWDM). However due to the limited gain bandwidth of the EDFA only a small fraction of the low-loss window of silica optical fibre is used in current telecommunication systems. Doping silica optical fibres with other rare earths could overcome this though problems associated with the vibrational structure of silica prevent its effective use as an amplifier medium when doped with ions such as praseodymium, thulium and dysprosium³. Another approach to accessing more of the low loss silica window is through using glasses doped with transition metals which have characteristically broad absorption and emission bands. However, the high phonon energy of silica glass results in emission from transition metal ions doped within it being quenched and leads to low quantum efficiencies.

A family of glasses that may be suitable for such applications are those based on sulphur, selenium or telluride (the chalcogenide glasses). Chalcogenide glasses have low phonon energies due to the relatively large atomic mass of their constituent atoms. In particular gallium lanthanum sulphide (GLS) glass has a maximum phonon energy of 425 cm⁻¹, which gives it excellent infrared transmission up 10.1 μ m (50% transmission)⁴. This low maximum phonon energy enables emission from many transitions within active ion dopants such as transition metals which are weakly or not at all observed in silica for example. Of particular interest are iron, nickel, chromium and cobalt which all exhibit broad infrared emission over the entire telecoms window leading to the possibility of a laser or optical amplifier for use in fibre optic communications, remote sensing and variety of medical, industrial and aerospace applications. Tuneable solid state lasers based on transition metal doped crystals have been demonstrated previously^{5,6}. However there are problems associated with producing active optical devices with these materials because in order to excite the transition metal ions and create a resonant cavity required to achieve lasing, optical systems must be designed and built using various components such as mirrors, filters, etc. Typically, the path length of the cavity is much longer than the gain region (i.e. length of the crystal) and so such devices are bulky, prone to thermal drift, and can be extremely difficult to align. Another problem is related to the short gain region that results in the need to use high

pump energies. This creates heat that in many cases acts as an efficient non-radiative quenching mechanism. As a result of this the transition metal doped crystal host must be actively cooled which becomes critical when attempting to obtain lasing at longer wavelengths (e.g. 2-5 micron). Incorporating such cooling systems into these systems is non-trivial as changing temperature affects the alignment of the cavity. Additionally, such cooling systems tend to add further 'bulk' to the system.

To overcome the issues associated with cavity alignment the use of a channel waveguide based system would be ideal. We have already demonstrated the ability to form low loss channel waveguides in GLS using a variety of techniques including direct UV and femtosecond laser writing⁴. Such systems would also allow highly efficient cooling due to the large active to non-active region ratio enhancing the ability to extract heat from the waveguide region. Such systems could also be significantly smaller than non-waveguide based devices. However, the formation of channel waveguide regions within crystals is in many cases not yet demonstrated and in those that have a non-trivial and expensive process, for example in Lithium Niobate⁷ and Ti:Sapphire⁸. Finally, the ability to use channel waveguides as the active region allows a much higher cross-section to be achieved thus significantly reducing the excitation energy required to achieve lasing. A highly compact device can be envisioned consisting of an inexpensive laser diode pump source coupled to a waveguiding gain region. In this paper we present spectroscopic data from iron, nickel, chromium and cobalt-doped GLS glass, our preliminary steps towards an amplifier and laser based on these promising materials.

2. Experimental

Samples of 0.031% iron, 0.017% nickel, 0.01% chromium and 0.017% cobalt (molar) doped GLS were prepared by mixing 65% gallium sulphide GaS_x ($x=1-1.5$), 30% lanthanum sulphide La_2S_3 , 5% lanthanum oxide La_2O_3 and the appropriate proportions of iron sulphide FeS , nickel sulphide NiS , chromium sulphide Cr_2S_3 and cobalt sulphide CoS_2 in a dry nitrogen-purged glovebox. Gallium and lanthanum sulphides were synthesised in-house from high purity gallium and lanthanum metal in a flowing H_2S gas system; the lanthanum oxide and vanadium sulphide were purchased from Merck and used without further purification. The glass was melted in a dry argon-purged furnace at 1150 °C for 24 hours before being quenched and annealed at 400 °C for 12 hours. The glass was then cut into 5 mm thick slabs and polished on two parallel faces.

Absorption spectra were obtained using a Varian Cary 500 spectrophotometer covering the 175-3300 nm spectral region. The system resolution was better than 0.5 nm in the UV-VIS and infrared region. The absorption spectra were obtained both with and without a reference sample as described in the text. Photoluminescence (PL) spectra were obtained using various laser excitation sources and dispersing the emission using a Bentham TMC300 monochromator. The dispersed emission was detected with a liquid nitrogen cooled InSb detector using standard phase sensitive detection. Low temperature PL spectra and emission lifetime measurements were carried out in an Oxford Instruments DN-V liquid nitrogen filled cold finger cryostat at 77 K. All spectra have been corrected for system response. Photoluminescence excitation (PLE) spectra were collected by placing a 1500 nm notch filter, with a full width half maximum (FWHM) of 20 nm, in front of the InGaS detector to select which wavelength of the emission was detected. To generate variable excitation energy a 250 W quartz halogen white light source was passed through the monochromator. The spectra were corrected for the varying intensity of exciting light (due to varying grating response and spectral output of the white light source) by measuring the excitation light with wavelength-calibrated Newport 818-SL and 818-IG detectors and a Newport 1830-c optical power meter.

Emission lifetime measurements were taken using a 1064 nm Nd:YAG laser modulated by an acousto-optic modulator (AOM). Emission was detected by a New Focus 2034 extended InGaS detector with a fall time of 5 μs .

3. Results

The transition metal compounds used to dope the GLS have the ions in the following oxidation states: Cr^{3+} , Fe^{2+} , Co^{4+} and Ni^{2+} . These oxidation states may remain in the finished glass but are likely to change because of the high temperature and reducing atmosphere of the glass-melting process. All absorption spectra show the absorption of the transition metal doped GLS and that of un-doped GLS for comparison. Figure 1 shows the absorption spectra of GLS doped with 0.01% chromium (molar) and un-doped GLS. Both are typical for GLS, showing a strong electronic absorption edge at around 500 nm, the chromium-doped sample shows a strong absorption peak at around 850 nm. The absorption of chromium-doped GLS has been investigated previously^{9,10} and similar results are reported, Brady cautiously attributed the absorption to Cr^{4+} and Petrovich attributed it to Cr^{2+} , Cr^{3+} and Cr^{4+} . The PLE spectra in

figure 2 shows two peaks at 700 nm and 1020 nm, this indicates that the observed broad absorption peak is due to two transitions. The PL spectra in figure 3 shows emission peaking at 1120 nm and 1320 nm when excited at 850 nm and 1064 nm which equates to an energy difference 1353 cm^{-1} between the emission peaks, which could suggest that the emission is coming from two different levels. Figure 4 shows the PL spectra for Cr:GLS at 77 K and 300 K, excited at 1064 nm. The emission peaks at 1320 nm and 1545 nm for temperatures of 300 K and 77 K respectively. This effect has been observed previously but with a smaller magnitude for Cr^{4+} -doped glasses^{11,12} and attributed to a combination of nonradiative decay and lattice expansion.

By comparison to the 15 K absorption spectra of Cr^{4+} -doped MgCaBa aluminate glass¹¹ and the spectroscopy of Cr^{4+} in other glasses¹²⁻¹⁴ and crystals^{15,16} we propose firstly that the chromium is in a 4+ oxidation state and the absorption and PLE peaks are due to $^3\text{A}_2(^3\text{F})$ to $^3\text{T}_1(^3\text{F})$, and $^3\text{A}_2(^3\text{F})$ to $^3\text{T}_2(^3\text{F})$ transitions. We also propose that the PL peak at 1120 nm from 850 nm excitation is due to the $^3\text{T}_1(^3\text{F})$ to $^3\text{A}_2(^3\text{F})$ transition and the PL peaks at 1320 nm from 1064 nm excitation is due to the $^3\text{T}_2(^3\text{F})$ to $^3\text{A}_2(^3\text{F})$ transition. This mechanism is illustrated in the configurational coordinate diagram for Cr^{4+} (figure 5), adapted from¹⁵.

Figure 1. Absorption spectra of 0.01% chromium-doped GLS and pure GLS.

Figure 2. Photoluminescence excitation spectra of 0.01% chromium-doped GLS.

Figure 3. Photoluminescence of 0.01% chromium-doped GLS at 300 K excited at different energies as shown.

Figure 4. Photoluminescence of 0.01% chromium-doped GLS at 300 K and 77 K excited at 1064 nm.

An emission lifetime measurement for Cr:GLS was attempted and was found to be less than the response time of the system (5 μ s). The 300 K emission lifetime for Cr:GLS has been measured previously¹⁷ to be ~ 1.2 μ s, this compares to 100 μ s for Cr⁴⁺:MgCaBa aluminate glass¹¹, 9 μ s for Cr⁴⁺:SrGaO₄¹² and 100 μ s for Cr⁴⁺:Li₂MgSiO₄¹².

Figure 5. Configuration coordinate diagram for Cr⁴⁺ with proposed transitions.

Figure 6 shows the absorption of Ni:GLS along with that of undoped GLS. The absorption of the nickel-doped sample peaks at around 1600 nm and is weak compared to the absorption of the chromium-doped sample, having a peak absorption coefficient of around 0.02 cm⁻¹ compared to 1 cm⁻¹ for chromium. The absorption bandedge of the nickel-doped sample is red-shifted in comparison to the undoped sample, indicating that there is a strong but unresolved absorption peak due to nickel ions in the bandedge region at around 500-600 nm. The absorption of nickel-doped GLS has been investigated previously and attributed to Ni²⁺⁹. The absorption of Ni²⁺-doped MgF₂ shows a strong absorption peak at around 400 nm due to the ³A₂(³F) to ³T₁(³P) transition along with two less intense peaks at 800 nm and 1400 nm due to the ³A₂(³F) to ³T₁(³F) and ³A₂(³F) to ³T₂(³F) transitions respectively¹⁸. Similar absorption peaks, attributed to the same transitions are also observed in Ni²⁺-doped MgAl₂O₄¹⁹. Since a glass host like GLS has a more inhomogeneous local field environment than a crystal host like MgF₂ one would expect the absorption bands of a dopant ion to become broader in the glass host. We therefore propose that the weak absorption peak at 1600 nm is due to both the ³A₂(³F) to ³T₁(³F) and ³A₂(³F) to ³T₂(³F) transitions and the strong unresolved absorption peak at around 500-600 nm is due to the ³A₂(³F) to ³T₁(³P) transition. The PL spectrum for Ni:GLS in figure 7 peaks at 1350 nm with a FWHM of 420 nm and since it is of higher energy than any of the observed absorption is most likely due to the ³T₁(³F) to ³A₂(³F) transition.

Figure 6. Absorption spectra of 0.017% nickel-doped GLS and pure GLS.

Figure 7. Photoluminescence of 0.017% nickel-doped GLS at 300 K excited at 1064 nm

Figure 8 shows the emission decay for nickel-doped GLS. The decay of emission can be exponential and therefore fit an equation of the form:

$$I(t) = I_0 e^{-\left(\frac{t}{\tau}\right)}$$

Where I_0 is the initial emission intensity and τ is the 1/e emission lifetime. However, it is frequently observed that the emission lifetime of ion doped glasses is non-exponential in nature^{20,21}. This is due to the random network structure of glasses resulting in each ion experiencing a slightly different local crystal field. The varying local environment experienced by each ion results in varying decay rates from ion to ion. The overall emission decay is therefore a sum of these different exponential decay rates. This continuous distribution of lifetimes can be described by a stretched exponential decay²², which has the mathematical expression:

$$I(t) = I_0 e^{-\left(\frac{t}{\tau}\right)^p}$$

Where p is the stretch parameter which describes the deviation from exponential behaviour. This stretched exponential was found to be the best fit for the emission decay of nickel-doped GLS, giving a 1/e lifetime of 40 μ s and a stretch factor of 0.42. This compares to 400 μ s for Ni^{2+} -doped MgAl_2O_4 ¹⁹

Figure 8. Emission decay of 0.017% nickel-doped GLS fitted with a stretched exponential.

Figure 9 shows the absorption of Co:GLS along with that of undoped GLS. The absorption of the cobalt-doped sample peaks at around 1400 nm. The absorption bandedge of the cobalt-doped sample is red-shifted in comparison to the undoped sample, indicating that there is a strong but unresolved absorption peak due to cobalt ions in the bandedge region. The absorption of cobalt-doped GLS has been investigated previously and attributed to Co^{2+} ⁹. The absorption of cobalt-doped gallium lanthanum sulphide oxide (GLSO) has been studied before and reveals an unresolved peak at around 650 nm⁹. By comparisons to cobalt-doped zinc chalcogenide crystals²³ we assign the unresolved peak to the $^4\text{A}_2(\text{F})$ to $^4\text{T}_1(\text{P})$ transition and the peak at 1400 nm to the $^4\text{A}_2(\text{F})$ to $^4\text{T}_1(\text{F})$ transition. The PL spectra for Co:GLS in figure 10 peaks at 1440 nm with a FWHM of 400 nm which also by comparison to²³ we assign to the $^4\text{T}_2(\text{F})$ to $^4\text{A}_2(\text{F})$ transition.

Figure 9. Absorption spectra of 0.017% cobalt-doped GLS and pure GLS

Figure 10. Photoluminescence of 0.017% cobalt-doped GLS at 300 K excited at 1064 nm

Figure 11. Absorption spectra of 0.031% iron-doped GLS and pure GLS.

Figure 12. Photoluminescence of 0.031% iron-doped GLS at 300 K excited at 1064 nm

Figure 9 shows the absorption of iron-doped GLS along with that of undoped GLS. The absorption of the iron-doped sample is strong and broad with three peaks observed at 1.35 μm , 2.0 μm and 2.7 μm . The absorption of Fe^{2+} -doped fluoride glass²⁴ show a double peak structure at 1 μm and 2.5 μm as does Fe^{2+} -doped alkali silicate glass²⁵ at 1.1 μm and 2.0 μm and Fe^{2+} -doped ZnSe at 3.0 μm and 3.7 μm ²⁶. The absorption of GLS doped with Fe_2O_3 (Fe^{3+}) exhibits a stronger absorption peak at 1.35 μm ⁹ this suggest that the absorption peaks at 2.0 μm and 2.7 μm are due to Fe^{2+} and the peak at 1.35 μm is due to Fe^{3+} . The PL spectra for iron-doped GLS in figure 12 peaks at 1460 nm with a FWHM of 430 nm. The peak positions and FWHM for the all photoluminescence spectra presented in this paper are given in table 1.

Dopant	Concentration (% molar)	Excitation wavelength (nm)	Temperature (K)	PL peak wavelength (nm)	FWHM (nm)
iron	0.031	1064	300	1460	430
nickel	0.017	1064	300	1350	420
cobalt	0.017	1064	300	1440	400
chromium	0.01	1064	300	1320	380
chromium	0.01	1064	77	1545	430
chromium	0.01	800	300	1120	520

Table 1. Photoluminescence peak positions and FWHM for various transition metal dopants, excitation wavelength and temperatures.

4. Conclusions

In this paper we report spectroscopic data for samples of 0.031% iron, 0.017% nickel, 0.01% chromium and 0.017% cobalt (molar) doped gallium lanthanum sulphide (GLS) glass. Photoluminescence (PL) with a full width half maximum (FWHM) of around 500 nm and peaking between 1120 nm and 1460 nm is observed when excited using excitation wavelengths of 850 nm and 1064 nm. The emission lifetime for nickel-doped GLS at 300 K was measured to be 40 μ s. Photoluminescence excitation (PLE) peaks for chromium-doped GLS at 700 nm and 1020 nm have been observed. By comparisons of our spectroscopic data to that of transition metals doped in other hosts we determine the oxidation state of the transition metal ions and propose transitions for the observed spectroscopic peaks. The long room temperature lifetime for nickel-doped GLS indicates the possibility of using this system to obtain laser action. However, further analysis in the form of excited state absorption and quantum efficiency measurements is needed to confirm this.

- 1 H. F. O. Humbach, U. Grzesik, U. Haken and W. Heitmann, *Journal of Non Crystalline Solids* **203**, 19-26 (1996).
- 2 J. Lucas, *Current Opinion in Solid State & Materials Science* **2**, 405-411 (1997).
- 3 J. Aronson, Thesis, University of Southampton, 2003.
- 4 A. Mairaj, Thesis, University of Southampton, 2002.
- 5 B. H. T. C. M. Stalder, M. Bass, *Appl. Phys. Lett.* **58** (1991).
- 6 L. L. C. S.A. Payne, H.W. Newkirk, L.K. Smith, W.F. Krupke, *IEEE J. Quantum Electron* **24** (1988).
- 7 J. P. K. Gallo, N.G.R. Broderick, D.J. Richardson, in *Proton-exchanged waveguides for photonic applications in lithium niobate*, 2004.
- 8 D. P. S. C. Grivas, T.C. May-Smith, R.W. Eason, M. Pollnau, in *Single transverse-mode laser operation of Ti:sapphire rib waveguides*, Lausanne, 2004.
- 9 M. N. Petrovich, Thesis, University of Southampton, 2003.
- 10 D. Brady, Thesis, University of Southampton, 1999.
- 11 X. Wu, *Journal of Non Crystalline Solids*, 120-126 (1996).
- 12 C. Anino, J. Thery, and D. Vivien, *Optical Materials*, 121-128 (1997).
- 13 X. Feng, *Optical Materials* **20**, 63-72 (2002).
- 14 S. Tanabe, *Applied Physics Letters* **77**, 818-820 (2000).
- 15 M. Grinberg, *Phys. Rev. B* **67** (2003).
- 16 H. L. W. Jia, S. Jaffe, *Physical Review B* **43**, 5234-5242 (1991).
- 17 C. R. Haythornthwaite, Thesis, University of Southampton, 1999.
- 18 S. Kück, *Appl. Phys. B*, 515-562 (2001).
- 19 N. V. Kuleshov, *Journal of Luminescence* **71**, 265-268 (1997).
- 20 M. J. Weber, *Physical Review B* **4**, 2932-2939 (1971).
- 21 A. Lempicki and R. M. a. S. R. C. Klein, *IEEE J. Quant. Electron* **14**(4) (1978).
- 22 K. Mullen, American Chemical Society (2003).
- 23 L. D. DeLoach and R. H. Page, *Journal of Quantum Electronics* **32**, 885-895 (1996).
- 24 S. M. Y. Ohishi, T. Kanamori, T. Manabe, *Physics and Chemistry Of Glasses* **24**, 135-140 (1983).
- 25 K. Fox, T. Furukawa, and W. White, *Phys. Chem. Of Glasses* **23**, 169-178 (1982).
- 26 J. J. Adams, C. Bibeau, R. H. Page, D. M. Krol, and L. H. Furu, *Optics Letters* **24**, 1720-1722 (1999).