Emission from a Bismuth Doped Chalcogenide Glass Spanning from 1 μm to 2.7 μm

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Abstract *We report emission from a bismuth doped chalcogenide glass with a full width half maximum of 850 nm. The quantum efficiency and lifetime were 32% and 175 μs. We report two new bismuth emission bands at 2000 and 2600 nm.*

Introduction

Bi doped glasses have been attracting considerable attention since broadband gain and laser action were reported around the telecoms window. Although there are numerous reports of Bi emission from traditional glasses we are only aware of one report of emission from a chalcogenide (GeS_2-Ga_2S_3)[1]. Chalcogenide glasses often exhibit low phonon energy. This allows the observation of certain radiative transitions in rare earth dopants that are not observed in traditional glasses such as silica. Gallium lanthanum sulphide (GLS) glass has a transmission window of ~0.5-10 μm, a refractive index of ~2.4 which results in high radiative emission rates, and a low maximum phonon energy of ~425 cm^{-1} which results in low non-radiative decay rates. In this work we report the absorption, excitation, emission (from excitation wavelengths of 480-1300 nm), quantum efficiency (QE), lifetime and cryogenic spectral measurements of Bi doped GLS (Bi:GLS).

Experimental

A sample of Bi:GLS was prepared by mixing 70% gallium sulphide, 23% lanthanum sulphide, 6% lanthanum oxide and 1% bismuth sulphide (% molar) in a dry-nitrogen purged glove box. Gallium and lanthanum sulphides were synthesised in-house from gallium metal (9N purity) and lanthanum fluoride (5N purity) precursors in a flowing H_2S gas system. Before sulphurisation lanthanum fluoride was purified and dehydrated in a dry-argon purged furnace at 1250 °C for 36 hours to reduce OH^- and transition metal impurities. The lanthanum oxide and bismuth sulphide were purchased commercially and used without further purification. Melt components were batched into a vitreous carbon crucible. The batch was then transferred to a furnace using a custom built closed atmosphere transfer pod. The glass was melted at 1150 °C for around 24 hours, in a silica tube furnace.

Absorption spectra were taken on a Perkin Elmer Lambda 900 spectrophotometer. Emission spectra were obtained by dispersing the fluorescence generated by laser sources in a Jasco CT-25C monochromator. The detectors were used were: a photomultiplier tube (PMT), an InGaAs detector and a mercury cadmium telluride (MCT) detector. These were coupled with standard phase sensitive detection. QE measurements were made using an integrating sphere and a “photons out / photons in” method, similar to that described in ref [2].

Results and Discussion

Fig. 1 shows a contour plot of emission from Bi:GLS at various excitation wavelengths. Two strong emission bands can be seen with excitation peaks at 680 and 850 nm. Two weaker emission bands can be seen with excitation peaks at 1020 and 1180 nm. These excitation peaks identify 4 absorption bands at 680, 850, 1020 and 1180 nm. This compares to absorption bands at ~500, 700, 800 and 1000 nm which are commonly observed in various Bi doped silicates and germanates[3]. This is the first observation of an 1180 nm absorption band in Bi doped glass. Fig. 2 shows the full width at half maximum (FWHM) of the emission spectra as a function of excitation wavelength. There is a strong dependence of FWHM on excitation wavelength. The most striking feature is the peak in FWHM at 1020 nm excitation, which coincides with the narrow 1020 nm absorption band identified in Fig. 1. Fig. 2 also shows the QE at various excitation wavelengths, the QE reaches a maximum of 32% with 900 nm excitation. Comparing the dependence of QE and FWHM indicates a trade-off between QE and FWHM.

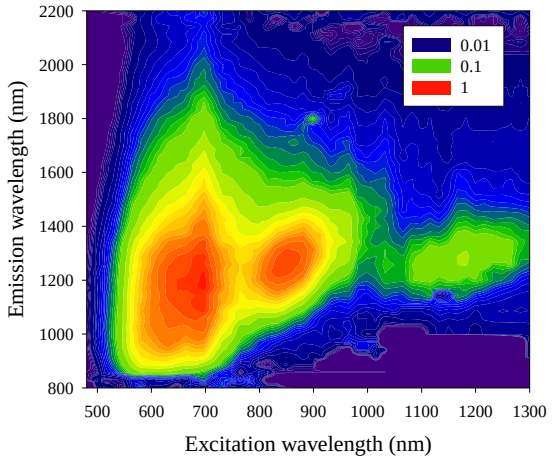

Fig. 1: Contour plot of emission at various excitation wavelengths

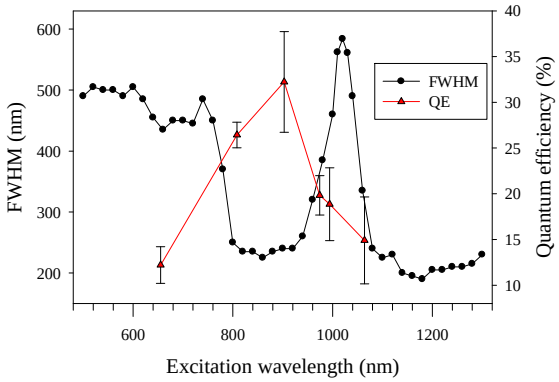

Fig. 2: Emission FWHM and quantum efficiency as a function of excitation wavelength

Examples of selected emission spectra, from excitation wavelength of 1064, 1020, 974 and 755 nm, are shown in Fig. 3. Excitation at 755 nm produces a single emission band peaking at 1220 nm with a FWHM of 482 nm. Excitation at 1064 nm produces a peak in a similar position except it is narrower and there is a second emission band at 1580 nm, a similar emission band was observed in Bi doped strontium-alumino-germanate glass[4]. When the excitation is 974 nm the peak shifts to 1350 nm. The emission from 1020 nm excitation is exceptional since it results in the largest FWHM of 600 nm and it covers the entire telecommunications window. The spectrum is also flattened over the O, E and S bands. The width of this emission equals the current broadest reported emission from a Bi doped glass which was from a Bi doped soda-lime-silicate glass excited at 720 nm[5]. However, the emission in ref [5] consisted of two rather separated peaks at 870 and 1200 nm and it did not cover any of the telecommunications window. The fact that this broad emission results from 1020 nm excitation is important because previous reports of lasing in Bi doped glasses tend to come from long excitation wavelengths. For example, the excitation wavelengths of various Bi doped glass lasers are 1070 nm [6] and 1080 nm [7]. The maximum lifetime was ~175 μs at emission and excitation wavelengths of ~1500 and 980 nm, respectively.

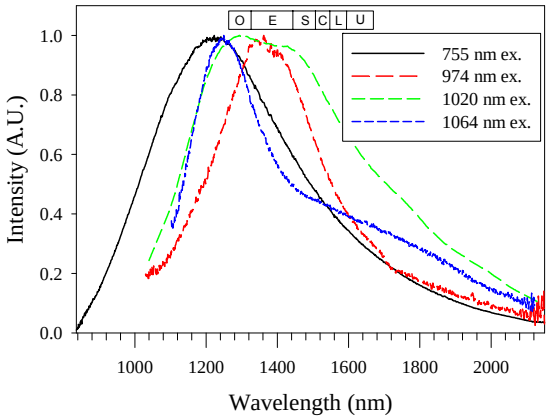

Fig. 3: Examples of emission spectra at various excitation wavelengths.

Fig. 4 shows the emission spectra from 974 nm excitation at temperatures of 5-300 K. As the temperature decreases new emission bands at ~1200 and 1500 nm appear to be formed, as well as longer wavelength emission bands.

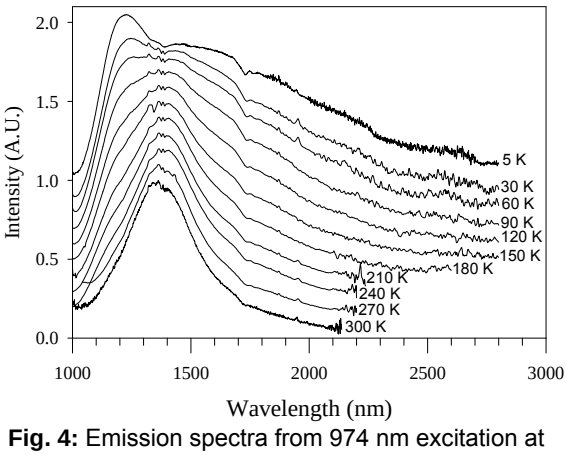

Fig. 4: Emission spectra from 974 nm excitation at temperatures 5-300 K

Fig. 5 shows the deconvolution of the emission spectrum at 5 K into Gaussians. The number of Gaussians was determined by the minimum number required to give a coefficient of determination (R^2) > 0.995. The deconvolution

reveals 4 Gaussian bands (1, 2, 3 and 4) centered at 1200, 1500, 2000 and 2600 nm, respectively. To the best of our knowledge this is the first time emission bands from Bi at 2000 and 2600 nm have been reported. We propose that the reason we are able to observe these low energy emission bands is a combination of the cryogenic temperatures and the unusually low phonon energy of GLS. In higher phonon energy glasses and at higher temperatures they may decay non-radiatively by coupling to phonon modes. The emission spectrum in Fig. 5 spans from 1 μm to 2.7 μm and has a FWHM of 850 nm. This is by far the broadest emission reported from Bi at any temperature and, to the best of our knowledge, the broadest emission from any active ion in this wavelength region.

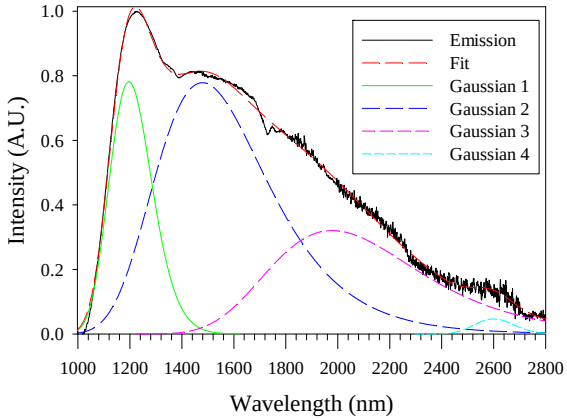

Fig. 5: Deconvolution of the emission spectrum at 5 K into Gaussians. Excitation was at 974 nm

We examined various published energy level models of Bi doped glasses to see if our emission bands at 2000 and 2600 could be accounted for. These models included a molecular orbital model of a BiO_4 molecule[8] and a model based on quantum-chemical calculations of Bi_2^- and Bi_2^{2-} dimers[9,10]. By examining the low-lying states of a Bi_2^{2-} dimer (Fig. 2, ref. 9) we found that the emission transitions $^1\Sigma_0 \rightarrow {}^3\Sigma_0^+$ and $^1\Sigma_0^- \rightarrow {}^3\Sigma_0^+$ appeared to have wavelengths of 1920 and 2330 nm, respectively. This is in reasonable agreement with the emission bands that we observed. It is the only model of Bi emission in glasses that we are aware of that can account for the 2000 and 2600 nm emission bands in Bi:GLS. We therefore propose that the origin of the emission in Bi:GLS is Bi_2^{2-} dimers.

Conclusions

In this paper we report for the first time, to the best of our knowledge, emission form a Bi doped glass with a FWHM of 600 nm which is flattened and covers the telecommunications window. The excitation wavelength and QE of this emission were 1020 nm and 17%, respectively. The maximum QE was 32% at 900 nm excitation. At cryogenic temperatures the FWHM reached 850 nm with 974 nm excitation, and we observed two new bismuth emission bands at 2000 and 2600 nm. Emission measurements taken with excitation wavelengths of 480-1300 nm revealed 4 absorption bands at 680, 850, 1020 and 1180 nm. The 1180 nm absorption band was previously unobserved. The maximum room temperature lifetime of 175 μs occurred at emission and excitation wavelengths of ~1500 and 980 nm, respectively. By examining previously published models of Bi emission in glasses to see if they could account for the 2000 and 2600 nm emission bands we propose that the origin of the emission in Bi:GLS is Bi_2^{2-} dimers.

References

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