VISIBLE UPCONVERSION IN RARE-EARTH DOPED GALLIUM LANTHANUM SULPHIDE BASED GLASSES

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Chalcogenide glasses are usually known for their good infrared and poor visible transparency which limit their applications to devices in the infrared wavelength region. Gallium lanthanum sulphide glasses, however, show visible transparency down to 500 nm. The low phonon energy of the glass increases the radiative quantum efficiency of rare-earth energy levels compared to commonly used fluorozirconate glasses and provides long-lived intermediate levels for efficient two-step excitation to visible energy levels. Green and red upconversion emission has been observed in Pr^{3+}, Nd^{3+}, Ho^{3+}, and Er^{3+} doped glasses under Ti:sapphire pumping in wavelengths regions where diode laser sources are easily available. Lifetime measurements reveal the excitation process is either excited-state absorption or upconversion caused by ion-ion interactions. Modification of the glass with lanthanum oxide or caesium chloride improves the visible transparency and shifts the UV absorption edge to 450 nm and 400 nm, respectively, and also improves the fibre drawing of these glasses.

1. INTRODUCTION

The development of compact sources of coherent visible radiation is currently receiving much attention for their applications in data storage, printing, video display, etc. One technique to generate visible radiation is the upconversion of infrared photons to visible photons in rare-earth (RE) doped glasses and crystals as it was first proposed and investigated by Auzel[1]. The RE ions can be promoted to higher visible energy levels by excited-state absorption (ESA) or upconversion by

ion-ion interactions. The upconversion efficiency is highest in host materials with low maximum phonon energies and hence low multiphonon decay rates for RE energy levels. These materials exhibit high radiative quantum efficiencies and long lifetimes for the visible energy levels and also for the intermediate energy levels, thereby increasing the probability for efficient two-step excitation. Since two infrared photons are required to generate one visible photon, high pump intensities are necessary for obtaining population inversion and laser operation in these systems. To date, the host material of choice for compact diode-pumped RE upconversion lasers is fluorozirconate glass fibre which combines a low phonon energy with a high pump intensity in the fibre core. Indeed diode pumped upconversion lasers in the red, green, and blue have been reported in praseodymium (Pr^{3+}), erbium (Er^{3+}), holmium (Ho^{3+}), and thulium (Tm^{3+}) doped fluorozirconate glass fibres[2-5]. However, a host material with a phonon energy lower still would be desirable for improving the efficiencies and reducing the threshold powers. Chalcogenide glasses, non-oxide glasses based on S, Se, or Te, have lower phonon energies but are commonly known for the restricted visible transparency. Se and Te based glasses are usually opaque, while some S based glasses have reasonable visible transparencies. In this paper we present initial data on visible upconversion emission from RE doped gallium lanthanum sulphide (GLS) glass.

2. EXPERIMENTS

Glasses were prepared by melting Ga_2S_3 and La_2S_3 powders in a vitreous carbon crucible inside a silica tube at about 1150°C for typically eight hours and quenching the melt to room temperature. The RE dopants were added to the melt in the form of the appropriate RE sulphide powder. The glass ingots were cut and polished either into square bulk samples for spectroscopic measurements or into rods and tubes for fibre drawing. Modified GLS glasses were fabricated by replacing all or part of the La_2S_3 with either La_2O_3 (GLSO) or CsCl (GLSCsCl)[6].

The UV absorption edge of undoped GLS and its modified versions were measured with a Perkin-Elmer Lambda-9 spectrometer. RE doped GLS glasses and fibres were excited with a tunable Ti:sapphire laser and an Ar^+ ion laser. The visible emission spectra were recorded with a liquid nitrogen cooled CCD spectrometer and fluorescence decay curves with a photomultiplier tube.

3. RESULTS AND DISCUSSION

Figure 1 shows the UV absorption edges of pure GLS glass and its two modified versions. GLS transmits down to a wavelength of 500 nm which can be considered as a good visible transparency compared to other chalcogenide glasses. Modification with La_2O_3 and CsCl clearly improves the visible transparency by shifting the UV absorption edge further into the blue. GLS glasses show a light brown colour while GLSO and GLSCsCl glasses are yellow and colourless, respectively. The addition of the modifiers also improves the fibre drawing properties of these glasses.

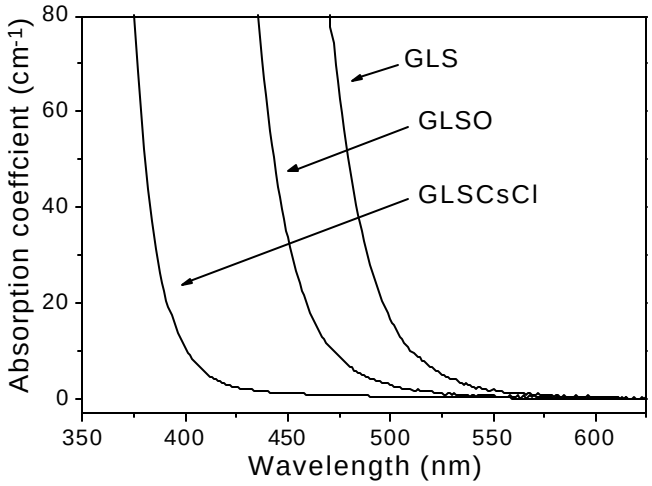

FIGURE 1

UV absorption edge of pure, La_2O_3 modified, and CsCl modified GLS glasses.

Visible upconversion emission has been observed from Pr^{3+}, Nd^{3+}, Ho^{3+}, and Er^{3+} doped GLS glasses for near-infrared Ti:sapphire pumping. Figure 2 and 3 show the measured emission spectra in the green and red wavelength ranges.The emission bands cover the regions from the blue end (490 nm) to the yellow end (570 nm) of

the green spectral range and from the orange end (600 nm) to the deep red end (680 nm) of the red spectral range. The shortest emission wavelength was obtained from Pr^{3+} at 490 nm. Shorter wavelength blue emission was not observed from pure GLS glass due to reabsorption by the strong fundamental glass absorption (Figure 1) but

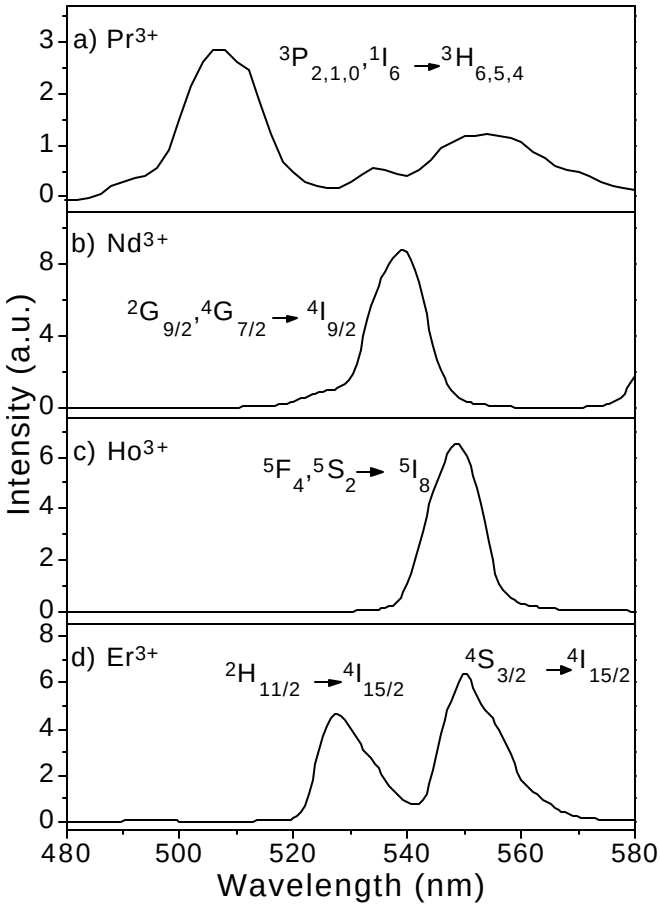

FIGURE 2
Green upconversion emission in GLS glass for
a) 0.05 mol% Pr_2S_3 pumped at 970 nm,
b) 0.05 mol% Nd_2S_3 pumped at 815 nm (fibre),
c) 1.5 mol% Ho_2S_3 pumped at 760 nm,
d) 1.5 mol% Er_2S_3 pumped at 805 nm.

is expected from oxide and halide modified glasses with improved transparencies in the blue.

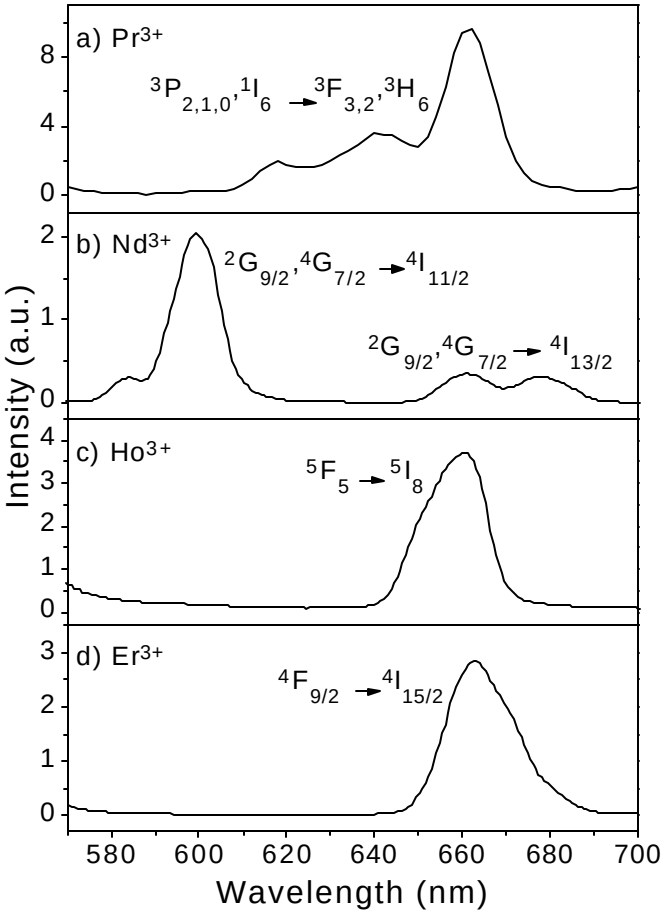

FIGURE 3
Red upconversion emission in GLS glass for the same samples and pump wavelengths as in figure 2.

The upconversion mechanisms for the visible emission bands are either excited-state absorption (ESA), ion-ion interaction or a combination of the two. They can be identified by measuring the ESA spectra and the visible fluorescence decay curves under direct and indirect excitation of the visible energy levels.

An example for upconversion by ion-ion interactions is the case of Nd^{3+} doped GLS. Two possible upconversion processes, u_1 and u_2, are indicated in figure 4. The Nd^{3+} ions are excited at 815 nm into the $^2H_{9/2}$,$^4F_{5/2}$ levels. Non-radiative decay populates the metastable $^4F_{3/2}$ level which is the upper laser level for the 1080 nm transition (1064 nm in YAG) and which has a lifetime of about 70 μs. Two

neighbouring Nd^{3+} ions in the $^4F_{3/2}$ level can exchange energy via the processes u_1 and u_2 leaving one ion in a lower state and one ion in the higher $^2G_{9/2}$,$^4G_{7/2}$ levels. The apparent energy mismatch is overcome by taking the width of the actual energy levels and the absorption and emission of phonons into account.[1] The nature of the upconversion process is also revealed by lifetime measurements of the visible levels under direct and indirect excitation. Direct excitation with an 514 nm Ar^+ ion laser gives a lifetime of 6 μs whereas upconversion pumping at 815 nm gives a lifetime

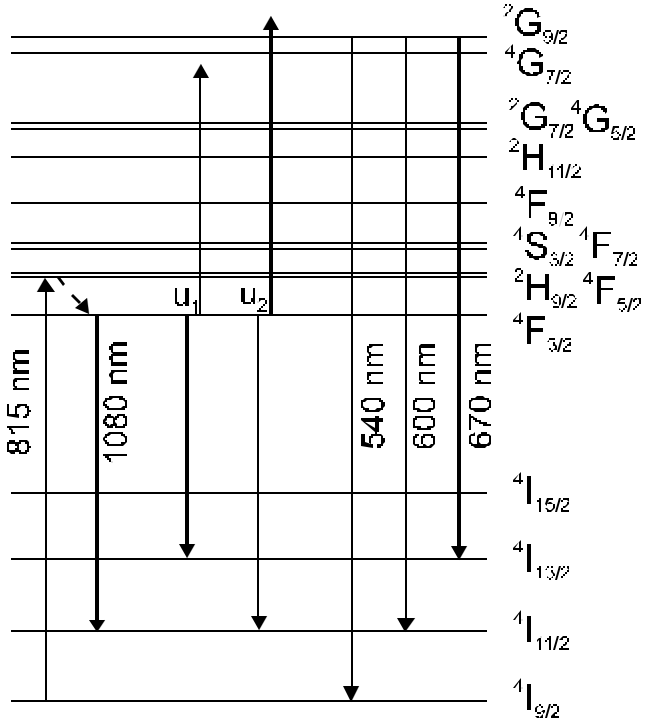

FIGURE 4
Nd^{3+} energy level diagram with infrared pump transition and possible upconversion processes u_1 and u_2 followed by visible emission

of about 30 μs. The lifetime under upconversion pumping corresponds to about half the lifetime of the metastable $^4F_{3/2}$ level and indicates that the visible levels are indeed populated by ion-ion upconversion between two ions in this level.

Absorption and fluorescence spectra along with results of 1080-nm laser experiments in Nd^{3+} doped GLS glasses and fibres can be found in Ref. 7 and 8.

An example for upconversion by ESA is shown in figure 5 for Ho^{3+} pumped at 760 nm. The absorption of the first pump photon populates the $^5I_4$ level and consequently the $^5I_{5,6,7}$ levels via radiative and non-radiative transitions. The absorption of the second photon promotes the same Ho^{3+} ion from the excited $^5I_7$ level to the $^5F_4$,$^5S_2$ levels.[9] For this excitation process the lifetime of the visible levels under direct and indirect pumping are expected to be equal. Indeed we

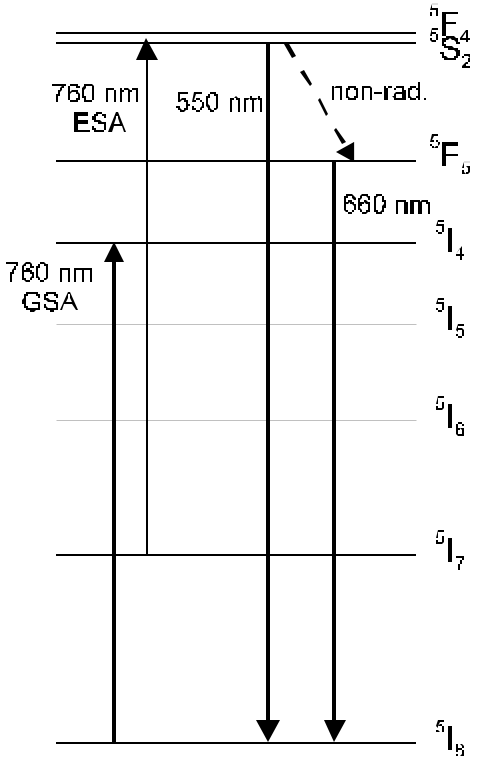

FIGURE 5
Ho^{3+} energy level diagram with pump transition for ground-state absorption (GSA) and excited-state absorption (ESA) followed by visible emission

measured a lifetime of 49 µs for 760 nm pumping which compares well to the 46 µs measured by Reisfeld[10] for 460 nm pumping and clearly shows that in this case ESA is the responsible process for the upconversion emission.

4. CONCLUSION

In conclusion we proposed RE doped GLS glasses and fibres as a new material for efficient upconversion of near-infrared light to visible light. Emission bands in the green and red were measured for four different RE ions. Modified GLS glasses show the potential for blue upconversion emission.

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