

# LOW PHONON-ENERGY GLASSES FOR EFFICIENT 1.3 μm OPTICAL FIBRE AMPLIFIERS

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The results of an experimental and theoretical study to compare the attributes of Pr<sup>3+</sup>-doped sulphide, chloride, mixed halide, fluoride and chlorotellurite glasses for 1.3 μm fibre amplifiers are presented. Quantum efficiencies based on measured and calculated radiative and nonradiative rates are presented for each glass together with its 1.3 μm fluorescence spectrum and an estimate of its loss.

**Introduction:** Currently there is immense interest in the development of glasses which offer lower maximum phonon energies and hence higher efficiencies than conventional fluorozirconate glasses for use in the commercially-important 1.3 μm optical fibre amplifier. The low quantum efficiency of the Pr<sup>3+</sup>-doped ZBLAN fibre amplifier, typically 3–4%, is a result of nonradiative, multiphonon decay from the <sup>1</sup>G<sub>4</sub> level to the underlying <sup>3</sup>F<sub>4</sub> level, which competes with the radiative emission at 1.3 μm [1]. The best reported [2] gain coefficient for a Pr<sup>3+</sup>-doped ZBLAN fibre amplifier is 0.21 dB/mW, which should be compared with the 11 dB/mW achieved for a 1.54 μm erbium-doped fibre [3].

To achieve an efficient 1.3 μm fibre amplifier we need to employ a lower phonon energy glass host in order to reduce the multiphonon relaxation rate between the <sup>1</sup>G<sub>4</sub> and lower-lying levels [4]. Chalcogenides and mixed halides of cadmium have been identified as providing significantly greater quantum efficiencies than ZBLAN [5–8]. The purpose of this Letter is to provide a critical analysis of these and other low phonon energy glasses as amplifier host materials.

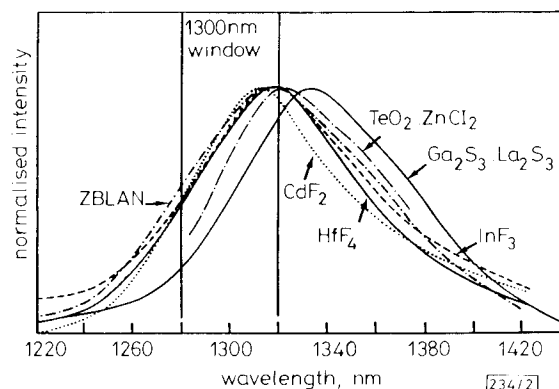
**Procedure:** As part of a long-standing programme, we have melted some 70 candidate low phonon-energy glasses, namely: sulphide, chloride, mixed halide, fluoride and chlorotellurite. The best glasses from among the candidate glasses were analysed spectroscopically for their potential as 1.3 μm amplifier hosts.

Fluorescence spectra and lifetimes were obtained by pumping with a Ti:sapphire laser tuned to the peak of the <sup>1</sup>G<sub>4</sub> ground-state absorption and analysing the emission. Raman spectroscopy on the undoped samples revealed the maximum phonon energy, from which the multiphonon decay rate could be calculated. Absorption data, combined with a calculation of Rayleigh scattering levels, provided an estimate of fibre intrinsic loss. Radiative decay rates were calculated from the absorption spectra of Pr<sup>3+</sup>-doped glasses using a Judd–Ofelt analysis.

**Results:** Analysis and comparison of Pr<sup>3+</sup>-doped candidate

glasses for their potential application as 1.3 μm amplifier hosts were based on three criteria: quantum efficiency for the <sup>1</sup>G<sub>4</sub>–<sup>3</sup>H<sub>5</sub> transition in Pr<sup>3+</sup>, fluorescence in the 1.3 μm telecommunications window and the potential for low intrinsic fibre loss at the pump and signal wavelengths of ~1.01 and ~1.3 μm, respectively.

**Quantum efficiency:** Comparison of the quantum efficiencies of the Pr<sup>3+</sup>-doped glasses requires the radiative and non-radiative rates from the <sup>1</sup>G<sub>4</sub> level in each host. Fig. 1 plots the calculated multiphonon lifetime for this level in each material.



**Fig. 1** Calculated multiphonon lifetimes as function of maximum phonon energy for each glass host

The dashed line indicates the trend of increasing lifetime and is not a theoretical result

This targets Ga<sub>2</sub>S<sub>3</sub>:La<sub>2</sub>S<sub>3</sub> and cadmium-based halides as hosts for which nonradiative decay will be minimised, these glasses having decay rates 70 and 30 times lower than ZrF<sub>4</sub>-based glasses.

Calculated radiative rates are summarised in Table 1, along with the measured total lifetimes of the <sup>1</sup>G<sub>4</sub> level. For the fluoride and tellurite glasses, the measured lifetime is dominated by multiphonon decay, whereas with the heavier halide glasses, radiative lifetimes begin to contribute to the total lifetime. For Ga<sub>2</sub>S<sub>3</sub>:La<sub>2</sub>S<sub>3</sub>, the radiative lifetime is further reduced and completely dominates the total lifetime. Unfortunately, the measured lifetimes for the CdCl<sub>2</sub>:CdF<sub>2</sub>, CdCl<sub>2</sub> and Ga<sub>2</sub>S<sub>3</sub>:La<sub>2</sub>S<sub>3</sub> glasses are all considerably lower than those predicted, an effect also observed by others [5, 6]. We attribute the discrepancy to the presence of OH<sup>-</sup> and other impurities which act to quench the measured <sup>1</sup>G<sub>4</sub> lifetime. The quantum efficiencies are given by the ratio of radiative rate to total decay rate of the <sup>1</sup>G<sub>4</sub> level and confirm the trends in Fig. 1.

**1.3 μm fluorescence structure:** Fig. 2 shows the fluorescence emission spectra for the range of glasses investigated. A drawback of the Ga<sub>2</sub>S<sub>3</sub>:La<sub>2</sub>S<sub>3</sub> glasses is that the peak of the emission and hence the expected gain is shifted away from the second low-loss window in silica fibres to the longer wavelength of 1334 nm. In comparison, ZBLAN and the other halide glasses, along with TeO<sub>2</sub>-ZnCl<sub>2</sub> have an emission

**Table 1** RADIATIVE AND NONRADIATIVE LIFETIMES FOR <sup>1</sup>G<sub>4</sub> LEVEL OF Pr<sup>3+</sup>

Glass	Radiative lifetime*	Nonradiative lifetime	Total lifetime**	Measured lifetime	Theoretical QE*	Measured QE*
	μs	μs	μs	μs	%	%
Ga <sub>2</sub> S <sub>3</sub> :La <sub>2</sub> S <sub>3</sub>	700	8440	650	180	93	26
CdCl <sub>2</sub>	2460†	3950	1520	80	62	3
CdCl <sub>2</sub> :CdF <sub>2</sub>	2460†	1020	721	105	29	4
CdF <sub>2</sub>	3210†	1020	774	184	24	6
InF <sub>3</sub>	4730	270	255	214	5	5
HfF <sub>4</sub>	3210†	110	106	135	3	4
ZrF <sub>4</sub>	3200	120	116	120	4	4
TeO <sub>2</sub> -ZnCl <sub>2</sub>	1800	8	8	—	0.4	—

\* ± 20% uncertainty in radiative lifetimes and quantum efficiencies

† Approximated using local-field correction

\*\* Total lifetime = τ<sub>R</sub>τ<sub>NR</sub>/(τ<sub>R</sub> + τ<sub>NR</sub>)

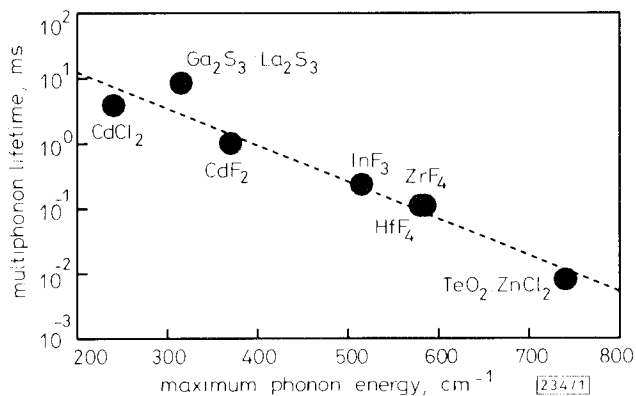
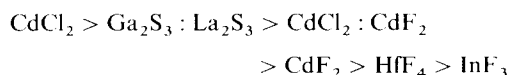


Fig. 2 Measured fluorescence spectra in second telecommunications window for  $\text{Pr}^{3+}$ -doped glasses

centred at 1320 nm. All spectra have a comparable bandwidth of  $\sim 90$  nm. The shift in the peak position of the fluorescence in  $\text{Ga}_2\text{S}_3:\text{La}_2\text{S}_3$  glasses compared with halide glasses arises because the former exhibit the nephelauxetic effect, i.e. are covalent in character, which results in a lowering of the energy levels of the rare earth ions.

**Fibre intrinsic losses:** All glasses showed transmission in the visible, with the  $\text{Ga}_2\text{S}_3:\text{La}_2\text{S}_3$  glasses having the longest wavelength cutoff of  $\sim 530$  nm. Although relatively long in wavelength, this visible transmission is exceptional among the chalcogenide family of glasses. Based on the position of the UV edge and taking into account Rayleigh scattering, all glasses had intrinsic losses in the second telecommunications window of less than 0.1 dB/m. In practice, measured losses were considerably larger than the intrinsic losses predicted and followed the trend



Losses in  $\text{CdCl}_2$  based glasses are due mainly to  $\text{OH}^-$  absorption. These samples quickly turned opaque after only a few minutes in air. High wavelength-independent scattering measured in our  $\text{Ga}_2\text{S}_3:\text{La}_2\text{S}_3$  glasses may result from internal disorder and defects, a consequence of incomplete glass annealing. These glasses however showed no devitrification or  $\text{OH}^-$  absorption after storage for over one year in the atmosphere of our laboratory.

**Conclusions:** The  $\text{Ga}_2\text{S}_3:\text{La}_2\text{S}_3$ ,  $\text{CdCl}_2$  and  $\text{CdCl}_2:\text{CdF}_2$  glass systems offer quantum efficiencies above 25%, a value which is considered to be the minimum for a viable 1.3  $\mu\text{m}$  optical amplifier. The  $\text{Ga}_2\text{S}_3:\text{La}_2\text{S}_3$  glass has the peak wavelength of the 1.3  $\mu\text{m}$  emission shifted away from the second telecommunications window. However,  $\text{Ga}_2\text{S}_3:\text{La}_2\text{S}_3$  glass is thermally and environmentally more stable than the chloride-

based glasses, which have relatively poor resistance to moisture, with  $\text{CdCl}_2$  glasses being the most susceptible to  $\text{OH}^-$  attack. All glasses show intrinsic losses in the 1  $\mu\text{m}$  region less than 0.1 dB/m and have the potential to form the low-loss optical fibres required for a practical 1.3  $\mu\text{m}$  amplifier.

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