

# CADMIUM MIXED HALIDE GLASS FOR OPTICAL AMPLIFICATION AT 1.3 $\mu$ m

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## ABSTRACT

Optical and spectroscopic data and calculations in support of an efficient 1.3  $\mu$ m amplifier in Pr<sup>3+</sup>-doped cadmium mixed halide glass host are presented. We find that the dominant parameter affecting the amplifier gain is the lifetime (325  $\mu$ s) of the Pr<sup>3+</sup>-<sup>1</sup>G<sub>4</sub> state. The long lifetime is the direct consequence of a decreased multiphonon decay rate in this low-phonon-energy glass host. We predict gain in excess of 30 dB for 100 mW pumping in low loss fibres, and for background loss of 1 dB/m, gain figures are as high as 15-20 dB.

## INTRODUCTION

Most land-based systems installed to date operate within the second telecommunications window centred at 1.3  $\mu$ m. The potential market for an amplifier operating at this wavelength is considerable. The characteristics for a 1.3  $\mu$ m amplifier could be met by an efficient praseodymium doped fibre amplifier (PDFA). When pumped at around 1  $\mu$ m (<sup>3</sup>H<sub>4</sub>  $\rightarrow$  <sup>1</sup>G<sub>4</sub>), Pr<sup>3+</sup>-doped fibres can amplify within the 1.3  $\mu$ m transmission window using the <sup>1</sup>G<sub>4</sub>  $\rightarrow$  <sup>3</sup>H<sub>5</sub> transition. Currently, state-of-the-art PDFAs are made from ZrF<sub>4</sub>-based ZBLAN fluoride fibres with quantum efficiencies typically lower than 4%.

Laser diode pumping is essential if 1.3  $\mu$ m fibre amplifiers are to be used in actual telecommunication systems. As the output power level from laser diodes is limited and operation of the laser diode at high power reduces the lifetime of the diode considerably, low pump powers are desirable and a high pump efficiency is required in order to construct a viable fibre amplifier. The performance of a PDFA depends on the optical properties of Pr<sup>3+</sup> in the host glass and the waveguiding properties of the fibre. Improving the waveguiding properties of ZBLAN fibres [1] have resulted in an optimized ZBLAN fibre with high numerical aperture, NA = 0.4, yielding the highest small signal gain coefficient yet reported of 0.21 dB/mW under standard pump configuration.

Our approach to improving the performance of the PDFA is to improve the optical properties of Pr<sup>3+</sup> by replacing ZBLAN with a lower phonon energy glass. The need for a low phonon energy glass stems from the fact that the lifetime of the <sup>1</sup>G<sub>4</sub> metastable level in existing Pr<sup>3+</sup>-doped ZBLAN glasses is dominated by multiphonon decay to the lower lying <sup>3</sup>F<sub>4</sub> energy level (an energy gap of 3000 cm<sup>-1</sup> typically) leading to low amplifier performance. Non-radiative decay (without the production of a 1.3  $\mu$ m photon) is mediated by multiphonon decay in which energy is lost to the glass matrix via excitation of phonons. The lower the phonon energy of the glass, the larger is the number of phonons required to bridge the <sup>1</sup>G<sub>4</sub>  $\rightarrow$  <sup>3</sup>F<sub>4</sub> energy gap and the lower is the non-radiative decay rate [2] making the transitions from the <sup>1</sup>G<sub>4</sub> metastable level predominantly radiative.

Cadmium mixed halide glasses with basic composition of CdX = 50CdF<sub>2</sub>-30NaCl-20BaCl<sub>2</sub> have lower phonon energies (as measured by Raman scattering) than ZBLAN glasses, 370 cm<sup>-1</sup> versus 580 cm<sup>-1</sup>. Our measured <sup>1</sup>G<sub>4</sub> lifetime (325  $\mu$ s compared to 110  $\mu$ s in ZBLAN) and estimated radiative lifetime using a semi-empirical modified Judd-Ofelt analysis predicts a quantum efficiency of 12%. This is a significant improvement over the 4% measured in ZBLAN-PDFAs and is the direct consequence of the decreased multiphonon decay rate.

Furthermore, our measurements show that changes in the various emission and absorption cross-sections that occurs between numerous halide glasses are small compared with the changes in the lifetime. As such, the dominant parameter affecting the amplifier gain is the lifetime of the  $^1G_4$  energy level. Using the measured  $^1G_4$  lifetime in CdX glass, our calculations show that a CdX-PDFA could have a small signal gain in excess of 30 dB for 100 mW of pump, and indeed with background losses as high as 1 dB/m would still yield a gain figure as high as 15-20 dB again for 100 mW of pump. This value of gain/pump is comparable to that obtained using the present state-of-the-art ZBLAN-PDFAs. Hence, any reduction in the background loss below 1 dB/m should result in a CdX-PDFA with a superior device performance to that achieved using ZBLAN.

In this paper, we present our optical and spectroscopic data and calculations in support of an efficient 1.3  $\mu\text{m}$  amplifier in a  $\text{Pr}^{3+}$ -doped cadmium mixed halide glass host. All CdX glasses were prepared at Brunel University. Thermal properties and characterisation of the glasses for suitability for fibre fabrication are discussed in separate papers in this special volume. Practical considerations for a 1.3  $\mu\text{m}$  PDFA device are glass phonon energy, transparency in the NIR, lifetime of the  $^1G_4$  level, fluorescence of the  $^1G_4 \rightarrow ^3H_5$  transition and excited-state absorption (ESA), ground-state-absorption (GSA) and amplified spontaneous emission (ASE), all at the signal wavelength.

### GLASS PHONON ENERGY

The vibrational spectrum of CdX glass from which the glass phonon energy can be identified was measured using Raman spectroscopy (excitation wavelength was 514.5 nm) as shown in Figure 1 [3,4]. It features Raman peaks at 240  $\text{cm}^{-1}$  and 370  $\text{cm}^{-1}$  associated with symmetric stretching modes of Cd-Cl and Cd-F respectively.

Unlike Raman spectroscopy, phonon-side-band (PSB) measurement identify the phonon energy of the crucial local phonons which couple directly to the rare-earth ions [5]. Sideband arise as a result of phonon-assisted absorption and appears as satellite peaks in an excitation spectrum. The phonon energy from our PSB measurement on  $\text{Eu}^{3+}$ -doped CdX corresponds to 280  $\text{cm}^{-1}$  as indicated in Figure 1, compared to the vibrational modes at 240  $\text{cm}^{-1}$  and 370  $\text{cm}^{-1}$  obtained by Raman scattering.

The Zr-F stretching vibrational mode in ZBLAN is at 580  $\text{cm}^{-1}$  and the PSB in ZBL is at 390  $\text{cm}^{-1}$  [6]. The number of phonons required to bridge the  $^1G_4$ - $^3F_4$  is at least 8 in CdX and 5 in ZBLAN. The non-radiative decay rate decreases by approximately an order of magnitude for each additional phonon.

There is an indication from the PSB result that the structural model proposed [7] for some cadmium mixed halide glasses also applies to CdX. Here, the smaller  $\text{F}^-$  anion acts mainly as bridging ions of the glass matrix and the larger  $\text{Cl}^-$  anion acts as nonbridging ions to which the rare-earth ions can coordinate with.

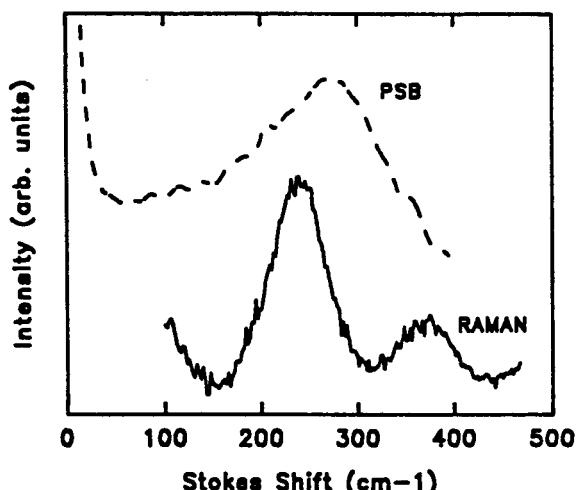


Figure 1: Raman and PSB for CdX

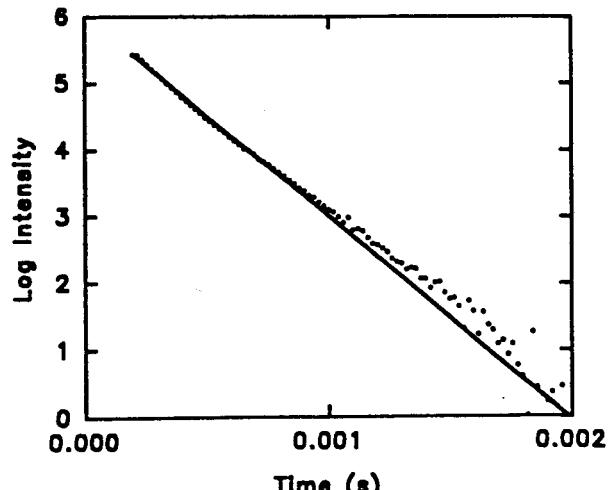


Figure 2: Decay Curve for CdX

PSB measurements also yield the electron-phonon coupling coefficient from the ratio of the areas under the main electronic transition and the PSB peaks. This parameter along with the phonon energy determine the non-radiative rate [2] and hence the quantum efficiency and signal gain. The ratio of the peaks in CdX reveals a value of 0.26 compared to 0.34 for fluorozirconate glass.

### INTRINSIC LOSS

A feature of halide glasses is their wide optical transmission range. Transmission and absorption measurements through a polished bulk glass sample provide the first indication of the suitability of a host glass for fibre application in the near infrared. CdX transmits in the range 0.5-10  $\mu\text{m}$ . The total intrinsic loss curve of CdX [4] taking into consideration the contributions from the UV absorption edge (Urbach), Rayleigh scattering and multiphonon absorption predicts an intrinsic loss at the 1.0  $\mu\text{m}$  pump wavelength of 0.01 dB/m and at the 1.3  $\mu\text{m}$  signal wavelength of 0.05 dB/m. In practice, our measured losses around 1.0  $\mu\text{m}$  were considerably larger than the intrinsic losses predicted due to impurities.

### LIFETIME MEASUREMENTS

A representative decay curve for CdX is shown in Figure 2. The lifetimes referred to in this text are derived from a single-exponential fit to the decay curve. The solid line in Figure 2 is the single-exponential fit to the data and we note the systematic deviation between the data and fit indicating a non-exponential decay. The possible physical explanations for a non-exponential decay are beyond the scope of this paper, however, it should be pointed out that we measure a similar degree of non-exponentiality in Pr<sup>3+</sup>-doped ZBLAN glass. Our longest measured lifetime is 328  $\mu\text{s}$  in CdX with 500ppm PrF<sub>3</sub> in a sample with the lowest level of impurities.

The Pr<sup>3+</sup> - <sup>1</sup>G<sub>4</sub> lifetime can be seriously reduced by the effects of concentration quenching, which in turn seriously degrades the performance of Pr<sup>3+</sup>-doped amplifiers through the reduction in the <sup>1</sup>G<sub>4</sub> lifetime. Figure 5 shows experimental results on a series of CdX samples doped with various levels of PrF<sub>3</sub>.

The measured lifetime is also affected by the presence of impurities. The presence of OH does not affect glass formation [8], however, it quenches the <sup>1</sup>G<sub>4</sub> - <sup>3</sup>H<sub>5</sub> transition. The dependence of the decay rate on OH concentration is linear in the range [OH] = 0.01-0.44 cm<sup>-1</sup>, <sup>1</sup>G<sub>4</sub> decay rate (s<sup>-1</sup>) = 3059 + 964x[OH] where [OH] is the peak of the far infrared absorption per cm around 3600 cm<sup>-1</sup>. The data extrapolates to 327  $\mu\text{m}$  at [OH] = 0.

### RADIATIVE LIFETIME

In order to quantify the quantum efficiency of the 1.3  $\mu\text{m}$  transition in CdX, the radiative lifetime of the <sup>1</sup>G<sub>4</sub> state is needed. Using our measured UV-VIS-NIR ground state absorption data from which the experimental oscillator strengths are derived (Table I), we have carried out a modified Judd-Ofelt analysis [9] of Pr<sup>3+</sup>-doped CdX glass. The modified Judd-Ofelt parameters are given in Table II, from which we calculate a <sup>1</sup>G<sub>4</sub> radiative lifetime of 2.87 ms. The quantum efficiency ( $\tau_{\text{measured}}/\tau_{\text{radiative}}$ ) is thus 11.5%.

The <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> states in Pr<sup>3+</sup> decay radiatively in CdX glass. The measured lifetimes for these states are 35  $\mu\text{s}$  and 335  $\mu\text{s}$  compared to the calculated values of 25  $\mu\text{s}$  and 289  $\mu\text{s}$  respectively. These results provide support for the Judd-Ofelt parameters derived from our fitting. An average error of 20% is indicated by our calculations [4].

Table I: Measured Oscillator Strengths of  $\text{Pr}^{3+}$  in ZBLAN and CdX Glasses  
All transitions are from the  ${}^3\text{H}_4$  ground-state level to the level indicated

Glass	Level	Experimental Oscillator Strength $\times 10^{-8}$							
		${}^3\text{P}_2$	${}^3\text{P}_1 + {}^1\text{I}_g$	${}^3\text{P}_0$	${}^1\text{D}_2$	${}^1\text{G}_4$	${}^3\text{F}_4$	${}^3\text{F}_3$	${}^3\text{F}_2$
		$\lambda(\text{nm})$	441	466	478	589	110	1441	1541
ZBLAN		1031	601	296	233	25	251	601	293
CdX		1463	487	343	212	14	311	584	50
									182

Table II: Modified Judd-Ofelt Parameters and Calculated Radiative Lifetimes for ZBLAN and CdX

Glass	Judd-Ofelt Parameters $\times 10^{-20} (\text{cm}^2)$				Radiative Lifetime ( $\mu\text{s}$ )		
	$\Omega_2'$	$\Omega_4'$	$\Omega_6'$	$\alpha \times 10^{-5}$	${}^1\text{G}_4$	${}^1\text{D}_2$	${}^3\text{P}_0$
ZBLAN	13.3	4.8	14.5	0.25	2880	241	37
CdX	5.0	3.8	18.8	0.27	2870	289	25

### EMISSION GAIN CURVE

Recently the  $1.3 \mu\text{m}$  ESA (due to  ${}^1\text{G}_4 \rightarrow {}^1\text{D}_2$ ) cross-section for  $\text{Pr}^{3+}$ -doped ZBLAN has been measured using a MCumber analysis on the  ${}^1\text{D}_2 \rightarrow {}^1\text{G}_4$  emission spectrum [10]. We have carried out a similar analysis on the mixed halide sample, the results of which are shown in Figure 3 along with our own measurements on a ZBLAN sample. The difference between the ESA and  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$  emission cross-sections yields a net cross-section which dictates the shape of the gain curve for the host glass. Comparing the values for ZBLAN and the mixed halide, we see that the peak of the gain is expected at  $1307 \text{ nm}$  in the mixed halide, some  $8 \text{ nm}$  shorter than our calculated value for ZBLAN. In the mixed-halide glass the peak cross-section is slightly smaller than the peak value in ZBLAN; due primarily to the increased linewidth in the mixed halide. The shorter operating wavelength is an advantage from the point of view of the GSA, attributed to the tail of the  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ .

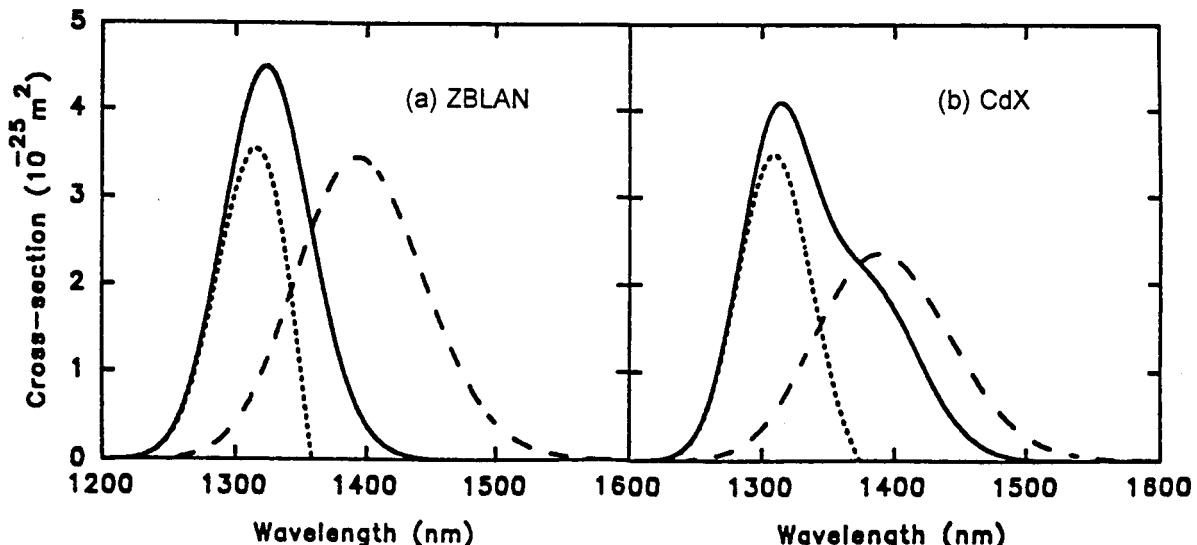


Figure 3: Measured  ${}^1\text{G}_4$  Emission Cross-Section and ESA for (a) ZBLAN and (b) CdX [11]  
Solid line = Emission; Broken Line = ESA; Dots = Gain Curve

## AMPLIFIER MODEL

The numerical model uses our own measured and calculated lifetimes and cross-sections to simulate the small-signal performance of a mixed halide glass amplifier operating at  $1.307 \mu\text{m}$ . The model includes the effects of GSA, ASE due to the  $^1\text{G}_4 \rightarrow ^3\text{H}_5$  transition, and the effects of ESA. The effects of bottlenecking at the  $^3\text{H}_5$  energy level are neglected because of the uncertainty in the non-radiative rates.

The rate equations for the relevant  $\text{Pr}^{3+}$  energy levels are solved alongside the equations describing the propagation of pump, signal and ASE (both forward and backward propagating) using routines developed for the erbium doped fibre amplifier. In comparing the amplifier performance of different halide glasses, we find that the dominant parameters determining the amplifier gain is the lifetime of the  $^1\text{G}_4$  energy level. Changes in the various emission and absorption cross sections that occur among the numerous halide glasses are small compared with changes in the lifetime. Consequently, an adequate comparison between the performance of  $1.3 \mu\text{m}$  PDFA based on ZBLAN, and other halide glasses can be obtained by using the accepted ZBLAN cross sections [12] and the  $^1\text{G}_4$  lifetimes measured in the bulk glasses.

Figure 4 shows our calculated amplifier performance for CdX device together with our ZBLAN results. We have compared the results of our modelling for ZBLAN with various experimental results [1,12] and found good agreement. These calculations are based upon  $^1\text{G}_4$  lifetimes for ZBLAN and CdX glasses of respectively 110 and 325  $\mu\text{s}$ . The fibre parameters are: NA = 0.4; cut-off wavelength = 880 nm; fibre length = 25 m;  $\text{Pr}^{3+}$  concentration = 500 ppm; background loss = 0.05 dB/m at both the pump and signal wavelengths. The small-signal gain values predicted for ZBLAN and CdX amplifiers are respectively 0.21 and 0.55 dB/mW.

The losses in high numerical aperture (NA) single mode fluoride fibres are extremely difficult to reduce below 0.1 dB/m at  $1 \mu\text{m}$ . As the background loss of the amplifier increases it becomes more important to keep the device length as short as possible. This can be achieved by increasing the concentration of  $\text{Pr}^{3+}$  ions, at a cost of reducing the  $^1\text{G}_4$  lifetime through ion-ion interactions. The effect of the  $\text{PrF}_3$  concentration on the measured lifetime has been studied in bulk CdX glasses and is shown in Figure 5. The line is a best fit to the measured data.

In order to minimise the effect of the background loss on the amplifier performance we run the model for each value of background loss and optimise the device length and  $\text{PrF}_3$  concentration using the lifetime data shown in Figure 5 to give the maximum small signal gain. The results of our numerical modelling are shown in Figures 6 and 7. The fibre parameters used in the calculations are: NA = 0.4, cut-off

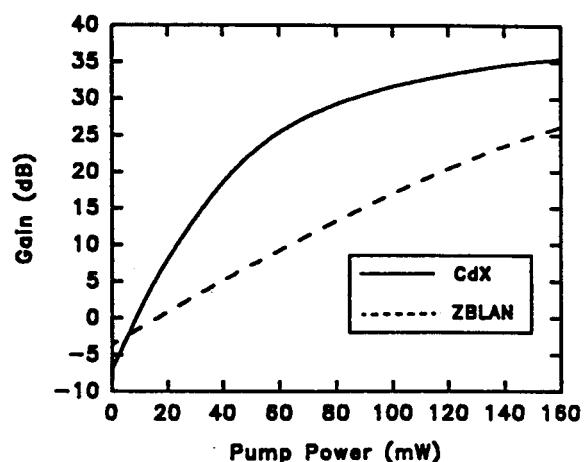


Figure 4: Calculated Gain in CdX and ZBLAN Fibres

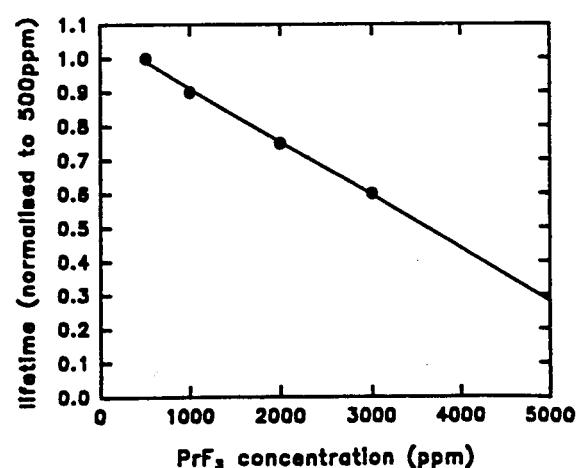


Figure 5: Lifetime versus  $\text{PrF}_3$  Concentration

wavelength 900 nm and pump power of 100 mW. The device length varies from 25 to 2 m as the  $\text{PrF}_3$  concentration increases.

The optimum  $\text{PrF}_3$  concentration as a function of the background loss is shown in Figure 6 and not surprisingly has a trend indicating that increasing the  $\text{PrF}_3$  concentration increases the background loss. We note the limited region, with background loss less than 0.1 dB/m, where a concentration of 1000 ppm or less is the optimum. Looking in detail at Figure 7 we see that with the optimum dopant concentration, amplifiers with background losses in the region of 1 dB/m can still have gain figures as high as 15-20 dB for 100 mW of pump. This value of gain/pump is comparable to that obtained using the present state of the art  $\text{Pr}^{3+}$ -doped ZBLAN fibre. Hence, any reduction in the background loss below this figure should result in a  $\text{Pr}^{3+}$ -doped CdX fibre amplifier with a superior device performance to that achieved using ZBLAN.

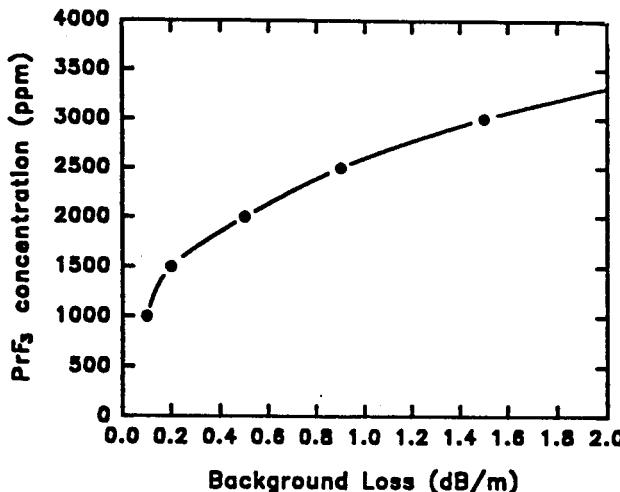


Figure 6:  $\text{PrF}_3$  Concentration versus Background Loss in CdX Fibre

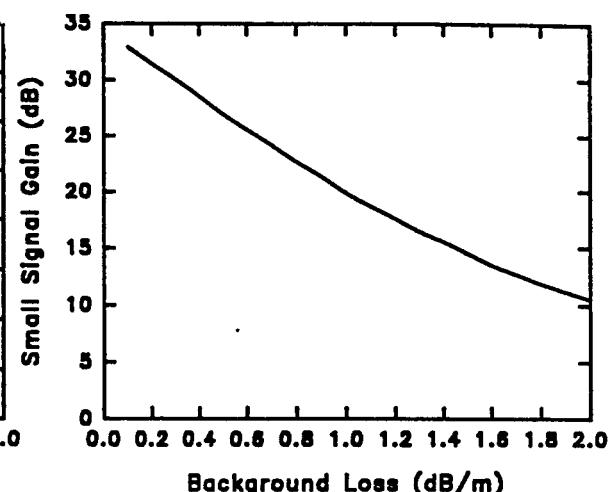


Figure 7: Gain in CdX Fibre versus Background Loss

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