True mid-infrared Pr³⁺ absorption cross-section in a selenide-chalcogenide host-glass.

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ABSTRACT

The mid-infrared (MIR) spans the 3-25 μ m wavelength range. Rare-earth-ion doped selenide-chalcogenide glasses are being developed for direct-emission MIR fibre lasers. The true Pr³⁺ absorption cross-section in the 3.5-6 μ m wavelength region of a Pr³⁺-doped (500 ppmw of Pr³⁺ *i.e.* 9.47 x 10¹⁹ Pr³⁺ ions cm⁻³) GeAsGaSe host-glass is presented, after numerically removing the underlying, extrinsic vibrational absorption due to [H-Se-] contamination of the host-glass.

Keywords: mid-infrared, chalcogenide glasses, rare earth ions, praseodymium ions, absorption cross-section.

1. INTRODUCTION

The chalcogenide glasses are based on the chalcogen elements: sulfur, selenium and tellurium, of Group XVI of the new Periodic Table, usually formulated with other elements, such as germanium, arsenic and antimony, to build up robust glass matrices that are mid-infrared (MIR) transmitting. The MIR spectral region spans the 3-25 μ m wavelength range. Chalcogenide glasses are attractive candidates for rare-earth-ion (RE) doped direct-emission MIR fibre lasers. This is because chalcogenide glasses offer: sufficient RE solubility; low intrinsic phonon energies (*down to ca. 250 cm⁻¹*) for efficient RE radiative processes and high refractive indices (*ca. 2.2-3.5*) for large RE absorption and emission cross-sections [1].

Fig. 1 shows the MIR absorption spectra of two bulk selenide-based chalcogenide glasses: a Pr^{3+} -doped GeAsGaSe core glass and an undoped GeAsGaSe/S cladding glass. The Pr^{3+} -doped GeAsGaSe core glass, doped with 500 ppmw Pr^{3+} (9.46 x 10¹⁹ ions cm⁻³), was directly drawn to unclad fibre for optical loss measurement across the MIR region; the fibre loss spectrum is shown here in Fig. 2(a)) [2].

The same Pr^{3+} -doped GeAsGaSe core glass and undoped GeAsGaSeS cladding glass, as presented in Fig. 1, were co-processed to make small-core, step-index fibre (SIF) [2]. This SIF exhibited Pr^{3+} photoluminescence (PL) from 3.5-6 µm wavelength and a long PL lifetime (7.8 ms) at 4.7 µm, similar to that found in the bulk core glass [2], demonstrating that the local environment of Pr^{3+} had been preserved in the fibre without RE clustering or glass-devitrification occurring, despite the intricate thermal processing required to make the SIF.

1.1 MIR vibrational absorption due to extrinsic [H] and [O] based host-glass impurities in RE-doped chalcogenide glasses

MIR extrinsic vibrational absorption bands, due to [H] and [O] based host-glass impurities, can underlie and be masked by RE MIR electronic absorption bands. At doping levels of a few 100s ppmw RE, this problem can lead to an inflated RE MIR absorption cross-section being wrongly inferred which, in turn, would lead to miscalculated RE emission cross-sections. By collecting MIR absorption spectra of chalcogenide glasses containing judiciously chosen RE, whereby the RE MIR absorption bands do not overlie particular extrinsic impurity vibrational absorption bands, the typical bandshape of the particular [H], [O], host-impurity absorption bands can be exposed and measured and this information then used to investigate analogous [H] and [O] impurity bands hidden from view under RE electronic absorption bands in spectra of other RE-doped glasses.

Focusing here on a Pr^{3+} -doped GeAsGaSe host-glass, we found that the MIR Pr^{3+} electronic absorption band spanning the 3.5-6 µm wavelength range, due to the ${}^{3}H_{4} \rightarrow {}^{3}H_{5}$ transition (Fig. 2(b)), obscured underlying vibrational absorption due to [H-Se-] which arose from unwanted [H] contamination in the host-glass. Unlike Pr^{3+} , Dy^{3+} has no ground state absorption in the 3.5-6 µm wavelength range. So the analogous vibrational absorption bands in the 3.5-6 µm wavelength range due to [H-Se-] contamination were left exposed in the MIR absorption spectrum of a Dy^{3+} -doped GeAsGaSe glass (see Fig. 3(a)). The [H-Se-] absorption bandshape of the Dy^{3+} -doped GeAsGaSe was measured and used to investigate the bandshape of the hidden [H-Se-] absorption in the spectrum of a Pr^{3+} -doped GeAsGaSe glass. This allowed us to establish the true Pr^{3+} MIR absorption crosssection in the ~3.5-6 µm wavelength range in a 500 ppmw (9.47 x 10¹⁹ ions cm³) Pr^{3+} doped GeAsGaSe host (Figs. 1 and 2(a)) by numerically removing the underlying extrinsic vibrational absorption due to [H-Se]. Two methods were used to do this. Firstly, in Method (i), the peak maximum absorption coefficient of each of the exposed [H-Se-] bands across the 3.5-6 μ m wavelength region in a Dy³⁺ doped GeAsGaSe bulk host-glass (Fig. 3(a)) were ratioed to give the [H-Se-] absorption bandshape. This absorption bandshape was then applied to investigate [H-Se-] vibrational bands in a Pr³⁺-doped GeAsGaSe glass spectrum. One of the [H-Se-] vibrational absorption bands was visible in the Pr³⁺-doped GeAsGaSe spectrum and so its peak absorption coefficient was used to calculate the absorption coefficient bandshape of the other [H-Se-] bands hidden from view, under the Pr³⁺ electronic absorption band. In this way, the combined {Pr³⁺ + [H-Se-]} absorption band in the Pr³⁺-doped GeAsGaSe glass (Fig. 2(a)) was deconvoluted into its component parts giving an estimation of the Pr³⁺ absorption cross-section.

In Method (ii), the exposed [H-Se-] bands in the 3.5-6 μ m wavelength region of the Dy³⁺-doped GeAsGaSe host-glass were Gaußian fitted. These Gaußian bands were fixed in ratio to fix the bandshape of the [H-Se-] absorption. Next the entire combined absorption band of {Pr³⁺ + [H-Se-]} in the 3.5-6 μ m wavelength region of the Pr³⁺-doped GeAsGaSe bulk glass [Fig. 1] was Gaußian fitted using the fixed ratio and other Gaußian bands to optimise the fitting. The observed absorption coefficient bandshape of the combined {Pr³⁺ + [H-Se-]} absorption band, was then deconvoluted into its component parts to give the Pr³⁺ absorption cross-section.

We compared these two methods and found that Method (ii) was more robust. The underlying [H-Se-] absorption cross-section was shown to be a substantial proportion of the observed $\{Pr^{3+}+[H-Se-]\}$ combined absorption cross-section in the Pr^{3+} -doped GeAsGaSe glass.

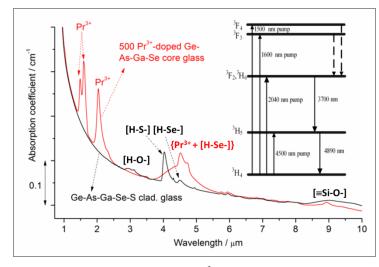


Figure 1. Red spectrum is the absorption spectrum of a Pr³⁺ doped GeAsGaSe core bulk glass from which was directly drawn unstructured fibre, whose absorption spectrum is given in Fig. 2(a)). The black spectrum is the absorption spectrum of a GeAsGaSeS cladding bulk glass. The Pr³⁺ doped GeAsGaSe core glass and undoped GeAsGaSeS cladding glass were used in the fabrication of a Pr³⁺-doped (500 ppmw Pr³⁺; 9.47 x 10⁻¹⁸ Pr³⁺ ions cm⁻³) small-core step-index, fibre [2]. (Inset [3] shows a simplified energy level diagram of the Pr³⁺-ion, with notional inter-level values.)

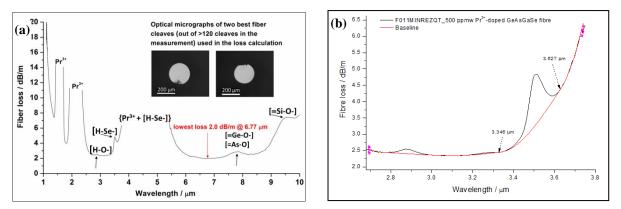


Figure 2. (a) Optical loss spectrum of a 500 ppmw Pr³⁺-doped GeAsGaSe unclad, intermediate fibre [2] drawn directly from the bulk core glass whose absorption spectrum is given in Fig. 1.

(b) Same as (a), but enlarged in order to show the problem of choosing a baseline for the satellite 3.5 μm [H-Se-] absorption band in Method (i). We found that errors in the choice of baseline position led to errors in the calculated Pr³⁺absorption cross-section.

2. METHOD (i): RATIOING OF UNMASKED [H-Se-] BAND TO THE MASKED [H-Se-] BANDS

The problem to solve is that MIR extrinsic vibrational absorption due to [H-Se-] overlaps and underlies the Pr^{3+} $^{3}H_{4} \rightarrow ^{3}H_{5}$ electronic absorption band, which spans the ~ 3.5-6 µm wavelength region (see Figs. 1, 2 [2]. Thus the true Pr^{3+} absorption coefficient bandshape (*i.e.* absorption cross-section) is unknown, especially at low doping levels of Pr^{3+} of the order 100s ppmw (~10¹⁸ ions cm⁻³).

Churbanov *et al.* [4] reported that the wavelength position of the maximum peak absorption coefficient of each of the three MIR vibrational absorption bands, due to [H-Se-], lying in the wavelength range 3.5-5.5 µm are at: 3.53 µm (weak), 4.12 µm (weak) and 4.57 (strong) µm. The 3.53 µm (weak) band lies on the periphery of, but appears distinct from, the 3.5-6 µm electronic absorption Pr^{3+} band (see Fig 2(a)); we will term this 3.53 µm [H-Se-] absorption a satellite [H-Se-] band. On the other hand, both the strongest vibrational absorption band of [H-Se-] (peak at 4.57 µm) and a weaker band due to [H-Se-] (peak at 4.12 µm) lie under the 3.5-6 µm electronic absorption Pr^{3+} band and are masked by it (Figs. 1 and 2(a)). The idea of Method (i) was to assume a constant ratio between the absorption coefficient at 3.53 µm (*i.e.* the maximum peak absorption coefficient of the weak, satellite (H-Se-) band) and any other absorption spectrum of a Dy^{3+} -doped GeAsGaSe glass [Fig. 3]. This is valid, for a particular glass-host, because all three absorption bands are due to the same atomic [H-Se-] impurity in the glass host. Each absorption band has a different extinction coefficient, because each band is manifested from a different vibrational symmetry of the [H-Se-] chemical bond.

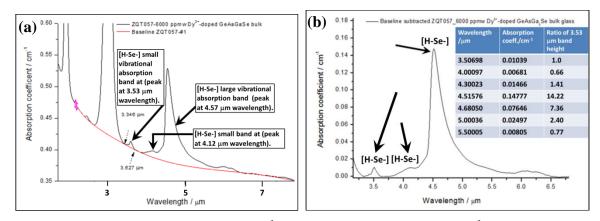


Figure 3. Absorption spectra of a 6000 ppmw Dy³⁺ doped GeAsGaSe bulk glass [5]. Dy³⁺ has no ground state absorption in the 3.5-6 µm range, leaving the three [H-Se-] absorption bands exposed in this spectral region. (a) A baseline (red) was fitted to the three [H-Se-] bands. For (b), the baseline loss in (a) was removed. Inset table in (b) shows the ratio of the absorption coefficient at the peak maximum of the 3.53 µm ([H-Se-] satellite band to the absorption coefficient at a series of wavelengths from ~3.5 to 5.5 µm

Therefore, we took the maximum peak absorption coefficient at 3.53 µm in the Dy³⁺ spectrum (see Fig. 3(b)), due to the [H-Se-] weak satellite band, and ratioed this to the absorption coefficient (excluding the baseline) due to [H-Se-] in the 3.5 to \leq 5.5 µm wavelength range to produce the tabulated values in the table-inset in Fig. 3(b). We then took the numerical loss of the 3.5 µm satellite [H-Se-] absorption band at its peak (Fig 2(b)) in the Pr³⁺-doped GaAsGaSe glass fibre and applied the calculated bandshape shown in the table-inset in Fig. 3(b). We assumed that the loss of the Pr³⁺-doped GaAsGaSe glass fibre was very similar to the loss of the bulk glass from which it had been drawn. The maximum peak of vibrational absorption loss due to [H-Se-] in the {Pr³⁺+[H-Se-]} combined absorption band was calculated to be 22 dB m⁻¹ at 4.52 µm in the bulk glass (Figs. 1 and 4). The maximum peak MIR electronic absorption loss of Pr³⁺ was inferred from this numerical fitting to be ~53 dB m⁻¹ at 4.52 µm wavelength (Fig. 4), instead of the originally observed, nominal value of 75 dB m⁻¹ at 4.52 µm of the {Pr³⁺ + [H-Se-]} combined band (Figs. 1 and 4).

Despite the Pr^{3+} and Dy^{3+} being dissolved in host glasses of similar GeAsGaSe composition, there still remains a question in Method (i) regarding the validity of assuming that the ratio of extinction coefficients of the three [H-Se-] absorption bands are constant in different host glasses and in the presence of different RE dopants. Moreover, during the numerical fitting we found that the [H-Se-] absorption coefficient bandshape in the range >3.5 µm to \leq 5.5 µm was very sensitive (estimated \pm 10 dB m⁻¹) to the numerical fitting of the baseline (see Fig. 2(b)) around the 3.5 µm satellite [H-Se-] band in the loss spectrum of the 500 ppmw Pr³⁺-doped GeAsGaSe hostglass fibre [2]. This problem arises because the 3.5 µm satellite [H-Se-] band tends to merge into the observed combined {Pr³⁺ + [H-Se-]} band.

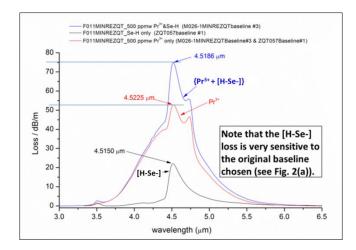


Figure 4. Optical loss spectra of Pr^{3+} -doped (500 ppmw Pr^{3+} ; 9.47x 10¹⁸ Pr^{3+} ions cm⁻³) GeAsGaSe host bulk glass showing: (blue) the originally measured, nominal absorption across the 3.5-6 µm, which is composed of both Pr^{3+} electronic absorption and [H-Se-] vibrational absorption and is denoted here as $\{Pr^{3+} + [H-Se-H]\}$; (black) the numerically modelled [H-Se-] vibrational absorption via applying [H-Se-] band absorption ratios taken from the absorption spectrum of a Dy^{3+} - doped GeAsGaSe bulk glass (see Fig. 3 (b)) and (red) calculated optical loss due only to Pr^{3+} electronic absorption i.e. the Pr^{3+} absorption cross-section in the 3.5-6 µm range.

3. METHOD (ii): GAUBIAN FITTING OF [H-Se-] ABSORPTION BANDS

Taking the Dy^{3+} absorption spectrum exhibiting [H-Se-] vibrational absorption in the 3.5-5.5 µm region (Fig. 3(a)), the spectral background was removed by selecting a best-fit baseline (Fig. 3(b)). The exposed H-Se MIR absorption bands after baseline removal (Fig. 3(b)) were fitted to a combination of Gaußian bands. Note that the abscissa was replotted in wavenumbers and the Gaußian equation, applied as follows:

$$f(x) = a. exp(\frac{-(x-b)^2}{2c^2})$$
(1)

where: x is wavenumber; a is maximum absorption coefficient; b is centre wavenumber of band; c is root-meansquare (RMS) bandwidth in wavenumbers. Eight Gaußians were summed to reproduce the [H-Se-] absorption spectrum in the Dy^{3+} -doped GeAsGaSe glass. The sum of the squares of the error between this generated spectrum and the actual [H-Se-] absorption spectrum was minimised using a Generalised Reduced Gradient (GRG) Nonlinear method in Excel Solver, allowing the a, b and c parameters to be adjusted to use a minimum number of Gaußians. The best fit was obtained with six Gaußians (Table 1 and Fig. 4). Note that the six Gaußians not only encompassed the satellite [H-Se-] band centred at 3.5 µm, but also include the satellite H₂O vibrational absorption due to molecular water bending centred at ~ 6.3 µm. The two Gaußians related to these two satellite bands were then removed to leave four Gaußian bands to model the two remaining [H-Se-] bands: *i.e.* those centred at 4.57 and 4.12 µm, respectively.

This 'best fit' four Gaußians were then kept in a strictly constant ratio. This strictly-kept ratio of four Gaußians was allowed to vary only in absolute terms (grow or shrink together) when used to help fit the observed combined $\{Pr^{3+} + [H-Se-]\}$ band of the Pr^{3+} -doped GeAsGaSe bulk glass (Fig. 3(a)) [2]; three more Gaußian bands [marked as 5, 6 and 7 on Fig. 5] were found necessary to model completely the combined $\{Pr^{3+} + [H-Se-]\}$ absorption band observed for the Pr^{3+} -doped GeAsGaSe bulk glass.

The software was allowed to choose impartially the relative scaling of these 3 extra Gaußians to the original four fixed-ratio Gaußians, there to represent the extrinsic [H-Se-] absorption at 4.57 and 5.12 µm wavelength.

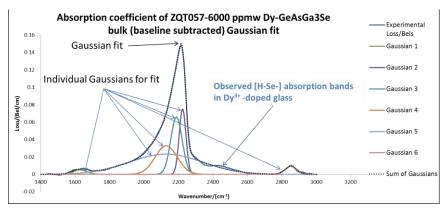


Figure 5. Absorption spectrum of a 6000 ppmw Dy³⁺ doped GeAsGaSe bulk glass [5] (cf. Fig. 3(b)) showing [H-Se-] absorption bands, replotted against wavenumber and fitted with six Gaußians (see Table 1) which included 4 to model the two[H-Se-] bands centred at 4.57 and 4.12 μ m (i.e. 2188 and 2427 cm⁻¹), respectively, and two more to model the two satellite bands ([H-Se-] centred at 3.5 μ m (2857 cm⁻¹) and H-O-H bend centred at ~ 6.3 μ m (1587 cm⁻¹), respectively.

Table 1. Six Gaußians used to model the [-H-Se-] absorption and H_2O bending absorption in the 3.5-6.5 μ m wavelength range of a 6000 ppmw Dy^{3+} doped GeAsGaSe bulk glass [5] (Fig. 4). (See equation 1 for a, b and c.)

1	Gaußian:	1	2	3	4	5	6
-	а	0.004941441	0.075042967	0.065949922	0.032897866	0.023233363	0.009322355
	b	1629.361887	2223.766372	2188.354826	2128.843047	2127.68845	2852.64625
	с	41.38943958	19.67724062	33.11283706	63.9764209	212.6234781	33.2451534

The Gaußian modelling (Fig. 6) gave an excellent fit to the { $Pr^{3+} + [H-Se-]$ } combined band absorption coefficient bandshape in the 3.5-6 µm region (as in Fig. 1), which helped validate the modelling. Gaußian fitting of the { $Pr^{3+} + [H-Se-]$ } combined band absorption coefficient bandshape in the 3.5-6 µm region of the Pr^{3+} doped GeAsGaSe bulk glass (Fig. 1) helped deconvolute this band [Fig. 6]. This deconvolution provided a means of separating the contributions of the Pr^{3+} electronic and [H-Se-] vibrational absorption bands to give the true Pr^{3+} absorption cross-section. The maximum peak of vibrational MIR absorption loss due to [H-Se-] was calculated to be ~35 dB m⁻¹ at 4.52 µm. We found Method (ii) less sensitive to baseline choice (Fig. 4) than Method (i) (Fig. 2).

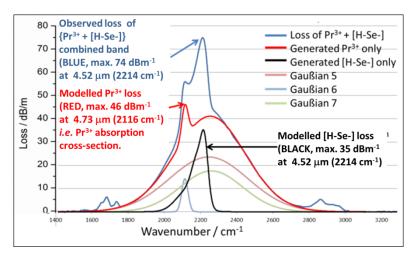


Figure 6. Optical loss spectra of a Pr³⁺-doped (500 ppmw Pr³⁺; 10¹⁹ ions cm¹⁹) GeAsGaSe bulk glass. Blue spectrum: observed, nominal absorption comprising both Pr³⁺ electronic absorption and [H-Se-] vibrational absorption denoted {Pr³⁺+ [H-Se-]}. Black: Gaußian modelled [H-Se-] vibrational absorption in the loss spectrum of a Dy³⁺- doped GeAsGaSe bulk glass (see Fig. 5) using four Gaußians which were then kept in constant ratio and allowed to grow or shrink together to generate the observed combined {Pr³⁺+ [H-Se-]} band shown in blue here. Red: calculated true Pr³⁺ absorption cross-section.

Importantly, Method (ii) modelling revealed a different bandshape for the Pr^{3+} absorption cross-section from that found in Method (i). For Method (ii), the Gaußian modelled Pr^{3+} maximum peak electronic absorption MIR optical loss had shifted to 4.73 µm wavelength (with loss 46 dB m⁻¹) *cf*. the originally observed combined band due to { Pr^{3+} + [H-Se-]}, with maximum peak MIR absorption at 4.52 µm wavelength (with loss of 74 dBm⁻¹).

Encouragingly, the Gaußian modelled Pr^{3+} bandshape was found to match that reported for more highly doped selenide chalcogenide glasses [6] where perhaps the Pr^{3+} electronic absorption was more dominating. We conclude that Method (ii) gives both a more accurate assessment of true Pr^{3+} absorption bandshape than Method (i) and a more accurate absorption coefficient bandshape, *i.e.* Pr^{3+} absorption cross-section.

4. DISCUSSION

Table 2 compares results from Methods (i) and (ii). Method (ii) was found less prone to errors of baseline judgement: estimated as *ca*. \pm 10 dB m⁻¹ for Method (i) in the calculated Pr³⁺ absorption cross-section from noting the influence of small changes in baseline on the estimated peak absorption loss of [H-Se-] in the 4-5.5 μ m band region. We 'guestimate' an analogous error of \pm 5 dB in the Pr³⁺ absorption cross-section in Method (ii). There remains a question over the validity of assuming a constant ratio of extinction coefficients for three [H-Se-] absorption bands (*i.e.* centred at 4.57, 4.12 and 3.53 μ m) in different hosts with different RE dopants in Method (i) and constant ratio of two [H-Se-] bands (4.57 and 4.12 μ m) in Method (ii).

Method (ii) gave a different, more accurate Pr^{3+} absorption bandshape than Method (i). Interestingly, it is the fact that the [H-Se-] vibrational absorption bandshape is different from, and distorts, the Pr^{3+} electronic absorption bandshape that lends the bands to Gaußian modelling

Therefore overall, Method (ii) gives a more accurate Pr^{3+} absorption cross-section than Method (i) for bulk selenide-chalcogenide glasses, and fibre, for Pr^{3+} doping levels of 100s ppmw (~ 10¹⁸ ions cm⁻³).

Table 2. Comparison of results of numerical modelling Methods (i) and (ii) of maximum peak absorption loss in Pr^{3+} -doped (500 ppmw Pr^{3+} ; 9.47 x $10^{18}Pr^{3+}$ ions cm⁻³) selenide-chalcogenide glass fibre.

	maximum loss and its wavelength position of the combined band {Pr ³ + [H-Se-]} absorption in the 3.5 - 6 μm range (Figs 1	peak loss / wavelength position of [H-Se-] underlying Pr ³⁺ absorption in a Pr ³⁺ - doped GeAsGaSe host-glass in the 3.5 –	/wavelength position of Pr^{3+} electronic absorption <i>i.e.</i> the Pr^{+3} absorption cross- section in a Pr^{3+} - doped GeAsGaSe	error in Pr ⁺³ loss in Pr ³⁺ - doped GeAsGaSe host-	Does calculated Pr ³⁺ bandshape match that in more heavily Pr ³⁺ doped chalcogenide glasses?
(i)	75 dB m ⁻¹ at 4.52 μm	20 dB m ⁻¹ at 4.52 μm (Fig. 4)	53 dB m ⁻¹ at 4.5 μm (Fig. 4)	$\pm 10 \text{ dB m}^{-1}$	No [6]
(ii)	75 dB m ⁻¹ at 4.52 μm	35 dB m ⁻¹ at 4.52 μm (Fig 6)	46 dB m ⁻¹ at 4.73 μm (Fig. 5)	$\pm 5 \text{ dB m}^{-1}$	Yes [6]

4. CONCLUSIONS

We conclude that the true Pr^{3+} absorption cross-section in selenide-chalcogenide host-glasses containing 9.47 x $10^{18} Pr^{3+}$ ions cm⁻³ (500 ppmw Pr^{3+}) is as depicted in Fig. 6; the maximum peak optical loss of Pr^{3+} was 46 ± 5 dB m⁻¹ at 4.73 µm wavelength. This true Pr^{3+} absorption cross-section should be used in future Judd-Ofelt modelling.

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