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Control of Absolute Quantum Yields in $NaYF_4$:Er,Yb Upconverters – Temperature and Power Dependence

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Experimental Setup for Absolute Quantum Yield (AQY) Measurements:

The setup used for the AQY measurements is shown in Figures S1 and S2. Figure S1 shows the movable holder and fibre-coupled integrating sphere (IS) used for holding the sample and the fibre-coupled laser used for excitation. Figure S2 shows the output from the IS-coupled fibre into an optical system which splits the beam (BS) sending part of the signal into an Oriel ¼ m 74100 monochromator and Oriel 77341 photomultiplier tube for analysis of the upconversion emission and part through a neutral density filter (OD 1.5) (to prevent saturation of the detector) and into a fibre coupled to an Ocean Optics Maya 2000 USB spectrometer, for analysis of the laser signal. The response of the system was calibrated in the range 300-1100 nm using an Oriel 63358 quartz tungsten halogen spectral irradiance standard. For the power-dependent study, the laser power was measured with a Spectra Physics 407A TC thermopile detector. The only spectrum measured with the PMT for each measurement was that with the sample directly in the beam, as no upconversion emission was detectable for any indirectly excited sample.

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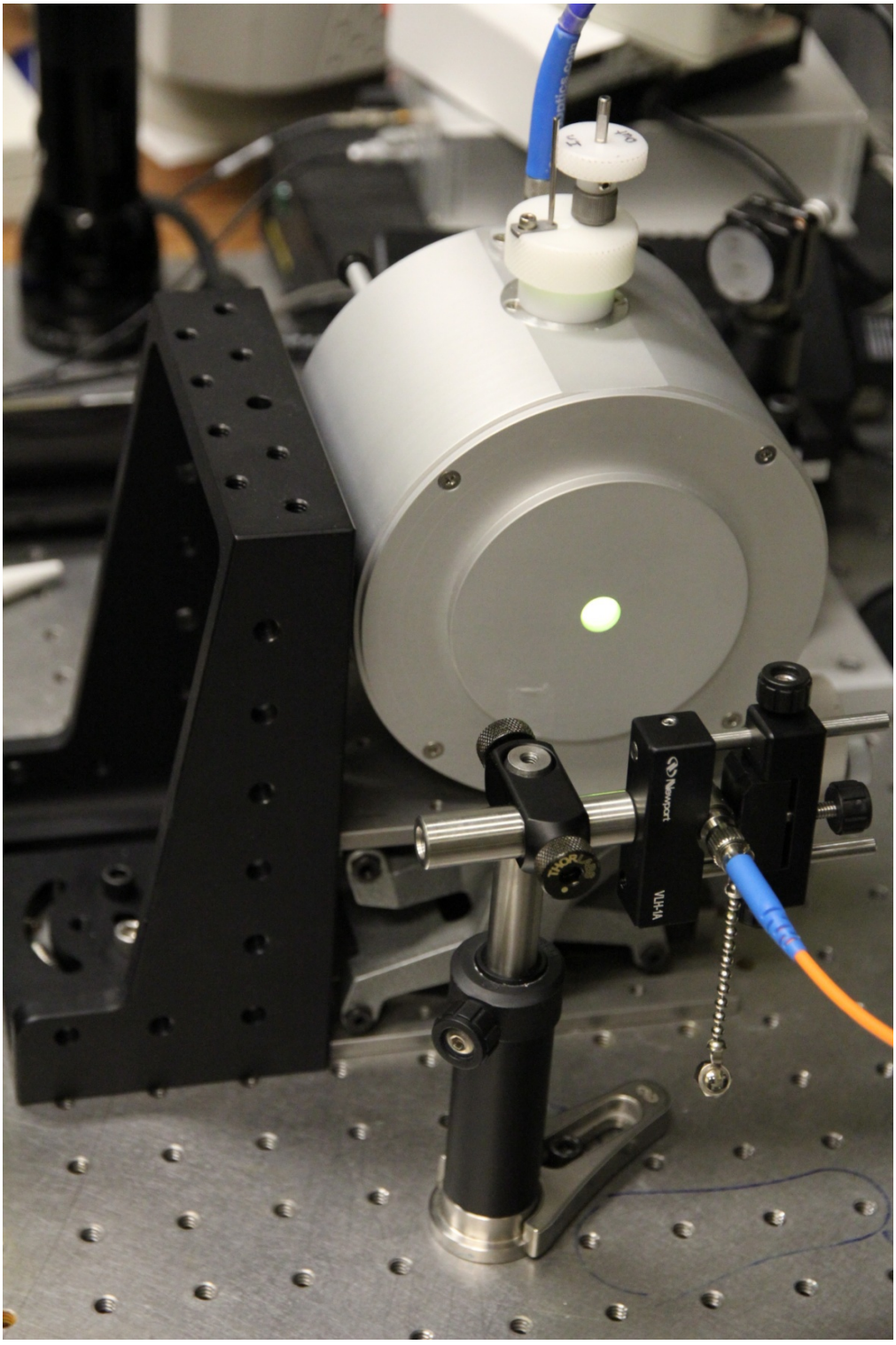

Figure S1. Fibre-coupled 972 nm laser (orange and blue) exciting an upconverter inside an integrating sphere. Light is collected by the blue fibre emerging from the top of the sphere.

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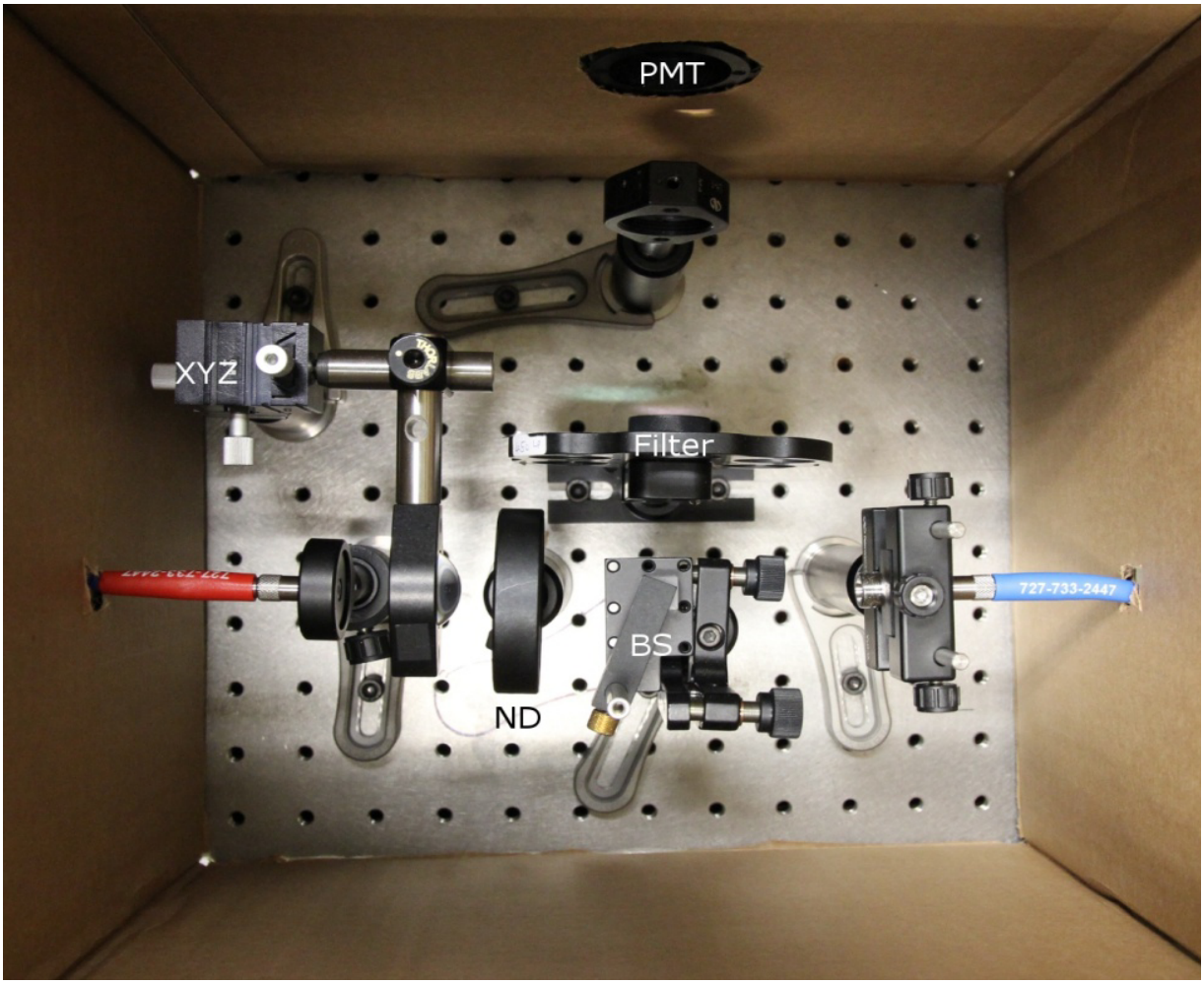

Figure S2. Light from the sphere emerges from the blue fibre, and is split at the beamsplitter (BS). One beam travels through a neutral density filter (ND) and is coupled in an Ocean Optics Maya Spectrometer via the red fibre. Light is focussed into the fibre by the lens mounted on an xyz stage (XYZ). The other beam passes through a filter which can be used to remove higher order peaks and is focussed into a monochromator and then to a photomultiplier tube (PMT) by a lens. The system is enclosed to shield it from external sources of light.

Synthesis of $NaYF_4$:Er,Yb Upconverters:

$NaYF_4$:Er,Yb upconveters were synthesized via thermal decomposition of 1.5 g of a mixed metal trifluoroacetate (TFA) precursor with an Na:Y:Yb:Er ratio of 1:0.78:0.2:0.02. The decompositions were performed in a quartz boat in a tube furnace in ambient air, and the

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formation of oxides was not observed, although some small amount of impurity yttrium oxyfluorite phase may exist at 700 °C. The TFA precursor was produced by dissolving yttrium, ytterbium, and erbium oxides and sodium TFA in excess aqueous trifluoroacetic acid (all purchased from Sigma) under reflux. After dissolution, excess water and trifluoroacetic acid were evaporated off and the precursor collected as a white solid. Approximately 40 g of precursor was produced and this same batch was used for all samples in the study. Before use the precursor was ground to a powder to maximise its homogeneity.

Figure S3 shows FTIR spectra of samples of $NaYF_4$:Er,Yb prepared at 250, 400 and 700 °C. It is evident that while significant organic residues are present at 250 °C, the samples prepared at 400 and 700 °C appear to be fairly clean and show very little evidence of organics.

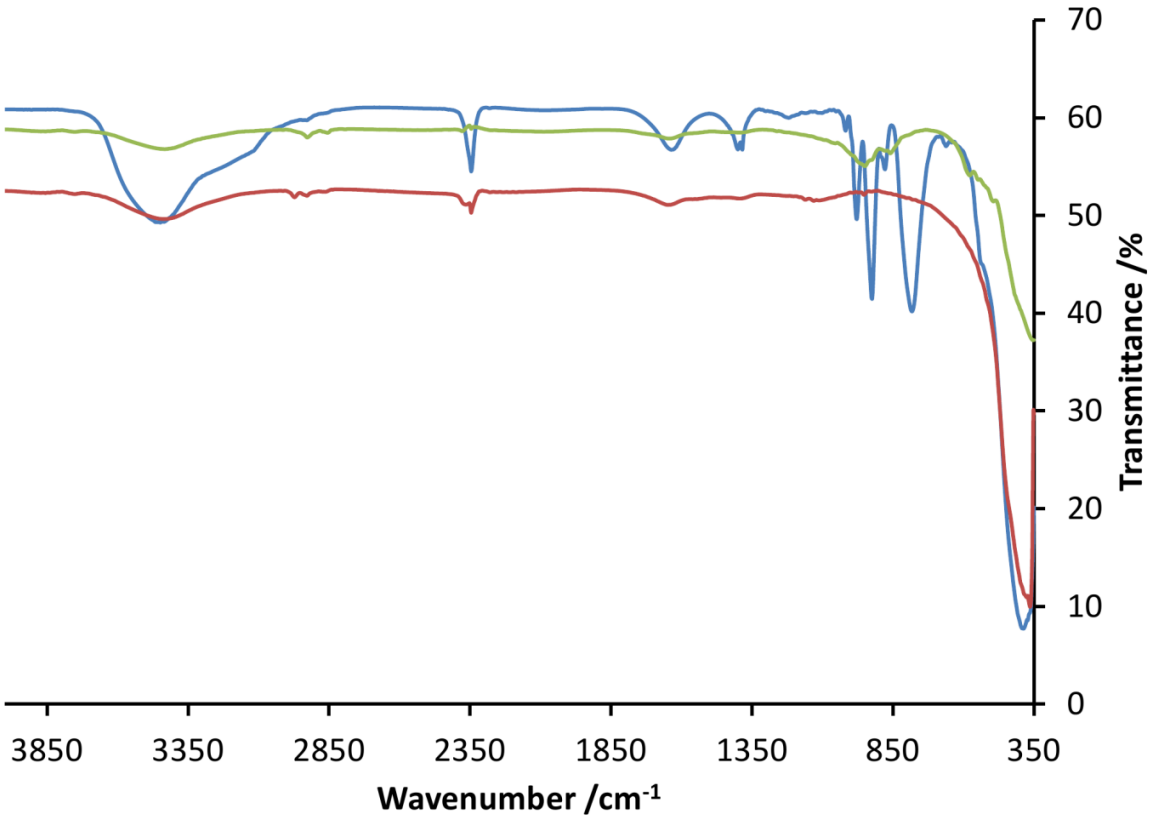

Figure S3. FTIR spectra of $NaYF_4$:Er,Yb prepared at 250 (blue), 400 (red) and 700 (green) °C.