Fluorescence from Yb^{3+} doped phosphate glass nano particles synthesized by pulsed laser ablation

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Coláiste na hOllscoile Corcaigh

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INTRODUCTION

Liquid Phase-Pulsed Laser Ablation (LP-PLA) is a well established technology for preparing colloidal solution of nano particles by irradiating targets with a pulsed laser beam in liquid [1]. This technique has advantages over the conventional synthesis methods: (i) the nano particles are formed easily and are collected with high efficiency, (ii) pure colloidal solutions can be prepared, compared with general chemical synthesis methods. Rare earth doped fluorescent nano materials have gained much attention in recent years because of their unique optical properties [2]. In this work, the second harmonic of a high power Nd:Glass laser at 527 nm (pulse width ~200 fs, repetition rate ~27 Hz) was used to generate NIR fluorescent glass nano particles. The laser had approximately 1.9 ± 0.1 mJ of energy per pulse (averaged over 30 seconds). The target was a phosphate glass doped with Ytterbium ($Yb^{3+}:P_2O_5$) immersed in Dimethyl Sulfoxide (DMSO).

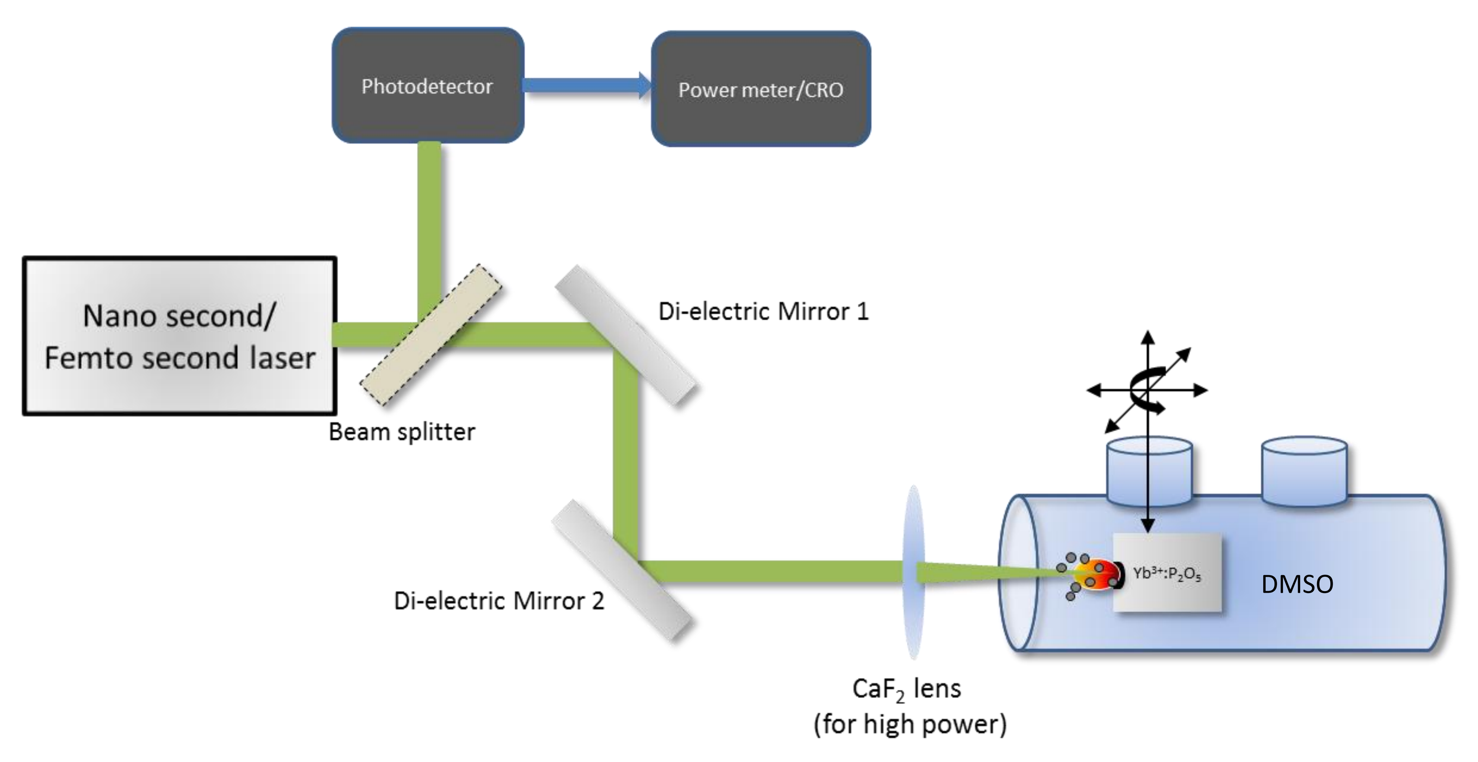


Fig. 1: Laser ablation set up for the generation of nano particles:

The NIR fluorescence nano particle suspension was studied upon excitation at different wavelength in the main absorption band using a home-made NIR fluorescence detection set up. When excited at the red edge of the absorption spectrum the Yb^{3+} ions in the glass can produce anti-Stokes (blue-shifted) emission. Anti-Stokes Emission (ASE) can potentially be used for light-driven cooling of the glass if the necessary conditions are met [3]. All cooling studies using ASE have been restricted to bulk samples. Theoretical studies on ASE in nano crystalline powders [4] confirm an enhanced cooling effect may be possible due to three main factors (i) Anderson localization of the pumping radiation (enhanced photon number) (ii) Increase in electron number by choosing optimal dopant concentration and (iii) enhanced phonon density of states (enhanced phonon number).

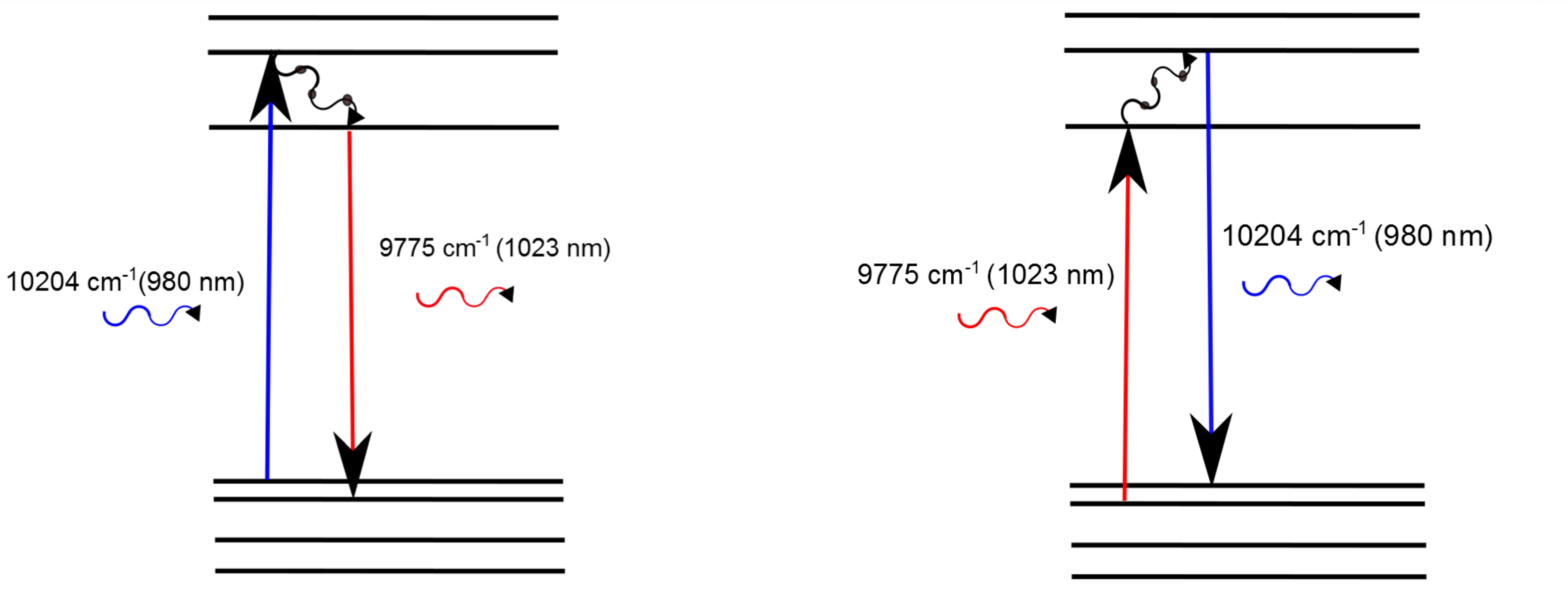
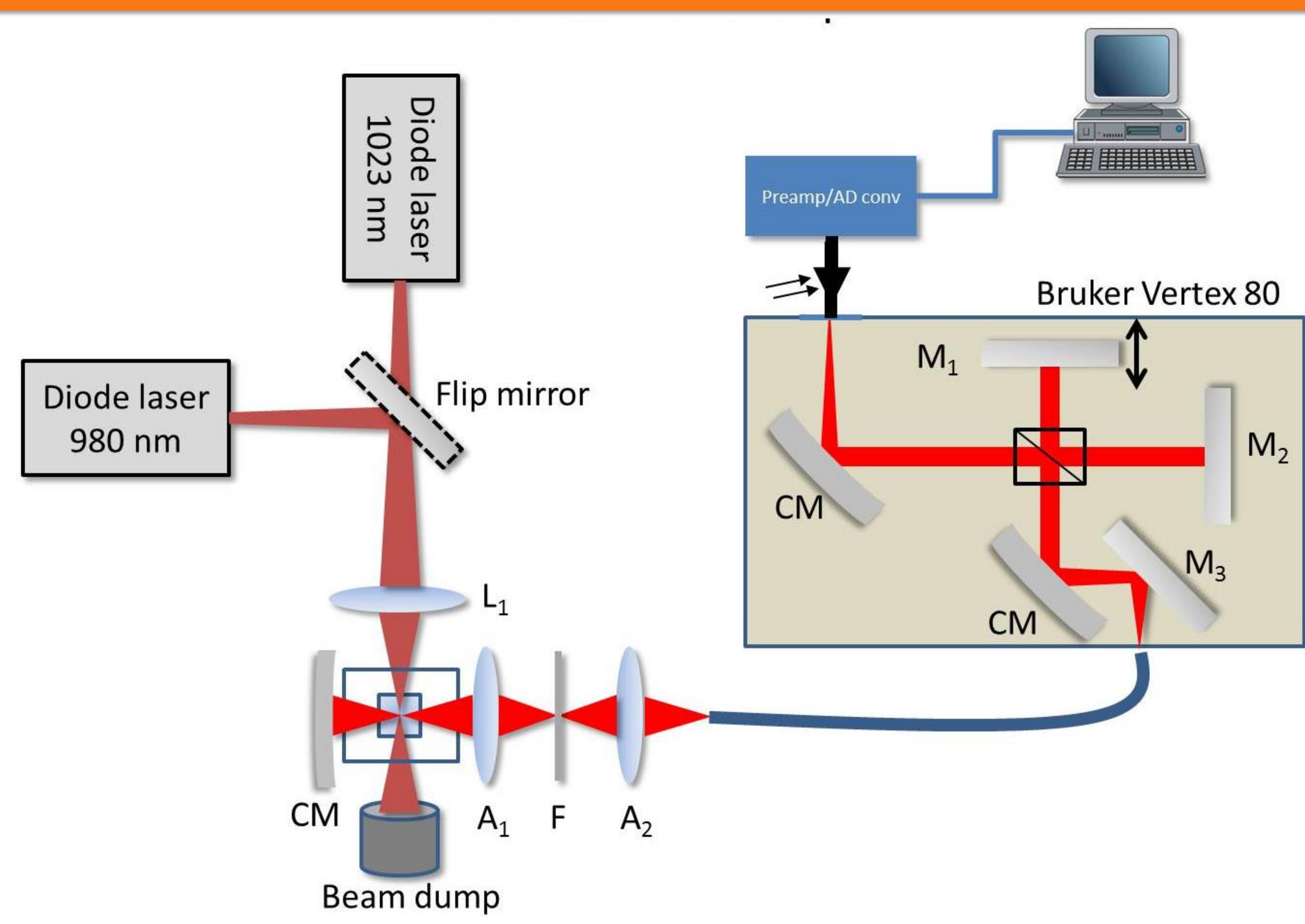


Fig. 2. Stokes fluorescence involves dissipation of energy of photon into the crystal lattice.
Fig. 3: Anti-Stokes fluorescence involves annihilation of a phonon resulting in a local cooling.

STUDY DESIGN



L- Biconvex lens, M- Flat mirror, CM- curved mirror, A- Achromatic lens, F- filter.

Fig. 4: Near Infra- Red fluorescence detection system schematic

Two continuous wave lasers in the near infra-red were used separately for excitation. A 100 mW laser (FU980AD200-BD12, Shenzhen Fuzhe Tech.) was used for excitation at 10204 cm^{-1} (980 nm) and a 20 mW laser (LD 1024 laser module, Frankfurt laser company) was used for excitation at 9775 cm^{-1} (1023 nm). A flip mirror was used for convenience in choosing the source. The fluorescence was collected using an anti-reflection coated achromatic lens and focused to a single strand fiber of 1.5 mm core (CS001xL03-08 AS1500-1650, Leoni Fiber Optics). The output of the fiber was coupled into a Fourier Transform spectrometer (FTS Bruker Vertex 80, maximum resolution 0.08 cm^{-1}) supplied with an InGaAs photodiode sensor. Fluorescence acquisition time used for generation of the spectra is 180 min.

RESULTS

- Nano particles of $Yb:P_2O_5$ were generated with sizes ranging from 200-300 nm. Photographs of the particles generated were taken using a Transmission Electron Microscope. Absorption spectra of the nano particles formed were recorded using a UV-Vis absorption spectrometer (Perkin-Elmer Lamda 1050).

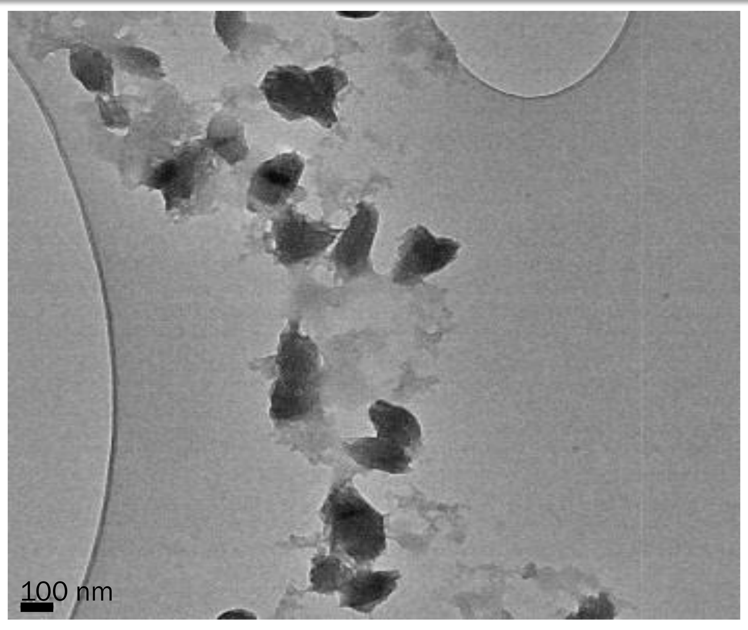


Fig. 5: TEM of synthesized $Yb^{3+}:P_2O_5$ nano particles

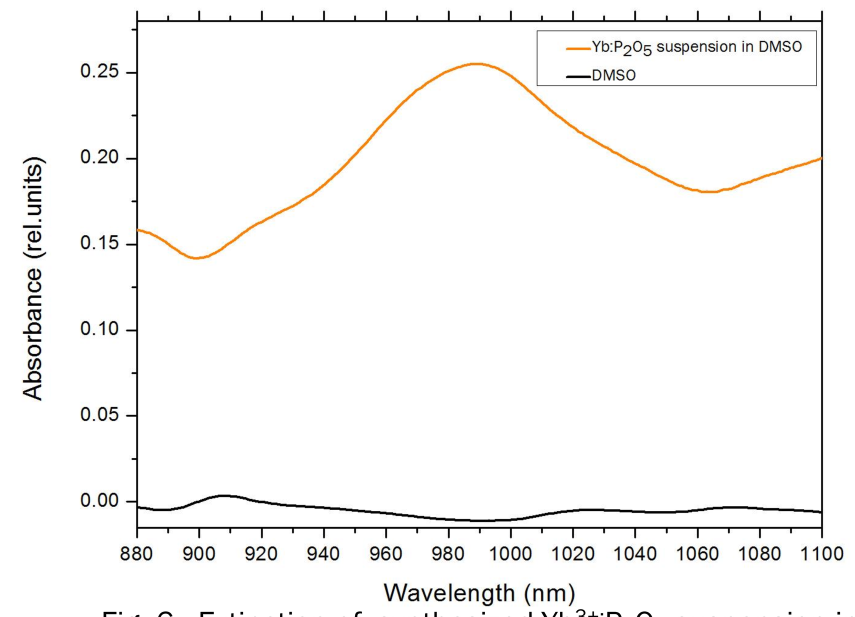


Fig. 6: Extinction of synthesized $Yb^{3+}:P_2O_5$ suspension in DMSO. Extinction from pure DMSO is shown as a reference.

- Fluorescence was recorded at two different excitation wavelengths, 1023 nm (Anti-Stokes) and 980 nm (Stokes)

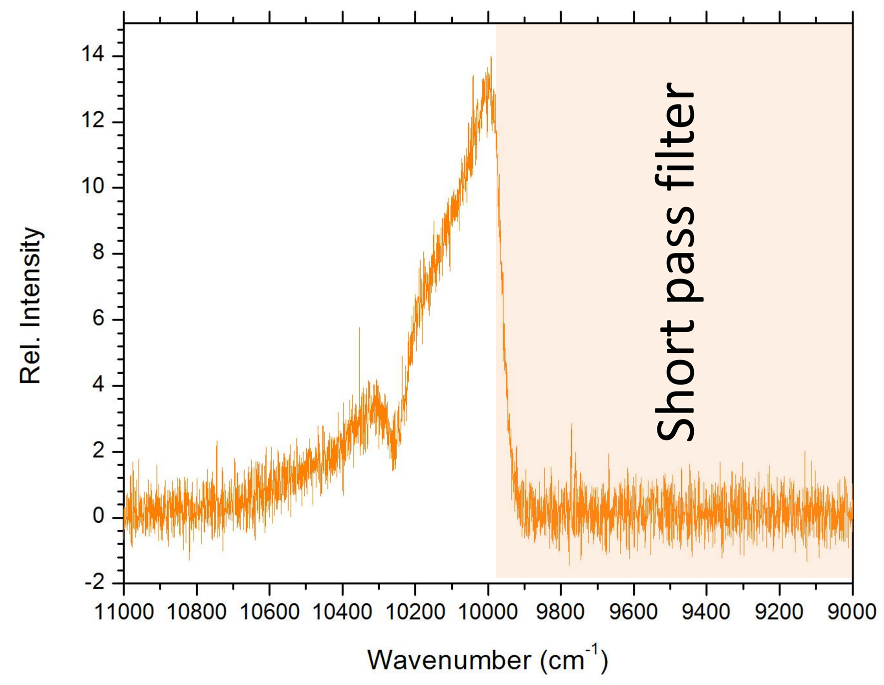


Fig. 7: Emission spectrum of $Yb^{3+}:P_2O_5$ nano partilce suspension upon excitation at 1023 nm

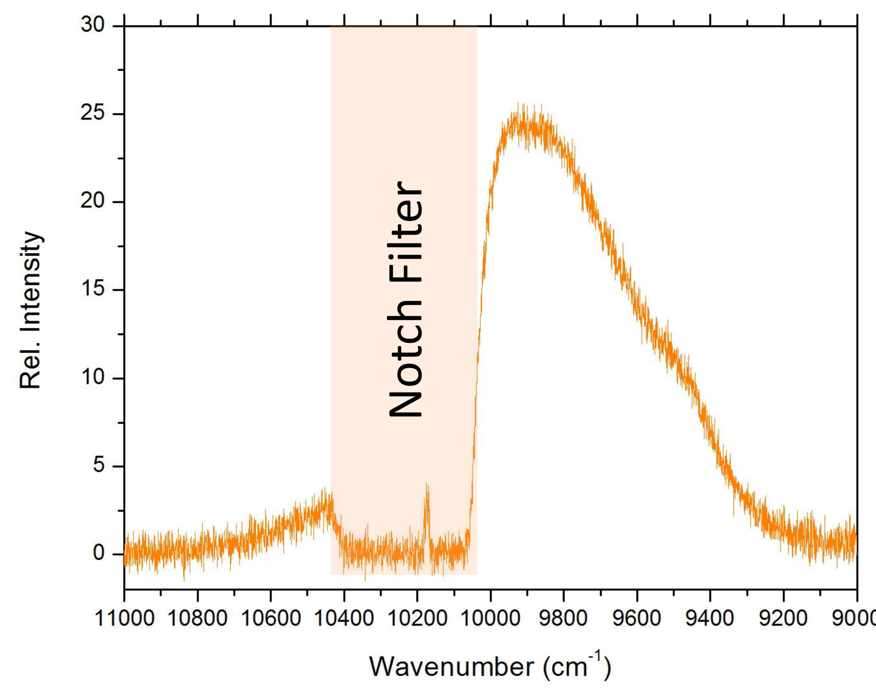


Fig. 8: Emission spectrum of $Yb^{3+}:P_2O_5$ nano partilce suspension upon excitation at 980 nm

DISCUSSION

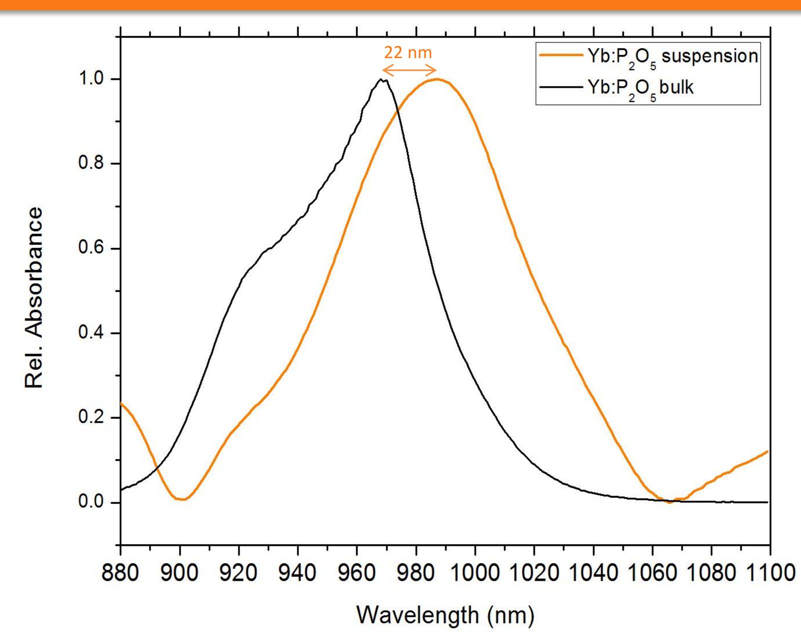


Fig.9: Normalized extinction curves for $Yb^{3+}:P_2O_5$ nano particle suspension and bulk $Yb^{3+}:P_2O_5$.

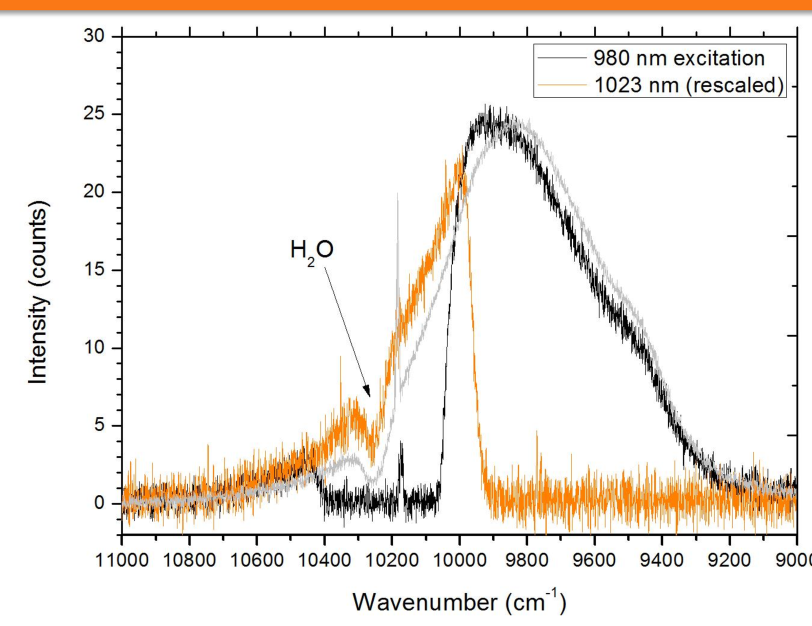


Fig. 10: Emission spectra upon excitation at λ_{exc} =1023 nm (orange, rescaled by factor 1.64) and λ_{exc} = 980 nm (black). Grey: fluorescence spectrum from the bulk (λ_{exc} = 980 nm).

Absorption spectrum: The normalized absorption spectrum of $Yb^{3+}:P_2O_5$ particle suspensions in DMSO exhibited a 22 nm red-shift compared to that of the bulk material against expectation. Both spectra were normalized to maximum extinction. A polynomial base line was subtracted from both the spectrum.

Emission spectra analysis:

- Dip at 10310 cm^{-1} is due to absorption from water molecules (ro-vibrational band at 975 nm) [5] present in DMSO. For the bulk, the same dip arises from the water molecules present on the surface of the glass due to its hygroscopic nature.
- The emission spectrum of the suspension at both excitation are blue shifted by 8 nm the particles when compared to that of the bulk.
- **The fluorescence of the nano particles upon excitation at 1023 nm (anti-Stokes excitation) was found to be around 6 times stronger than that upon excitation at 980 nm (Stokes excitation).** The normalized absorbance (Rayleigh scattering subtracted extinction) at 980 nm (0.09) and 1023 nm (0.04) showed that the absorption at 980 nm was 2.05 times stronger than at 1023 nm. The laser at 980 (100 mW) nm was 5 times stronger than the one used at 1023 nm (20 mW). This made the short-wavelength ca. 10 times more efficient than excitation at the long wavelength. The anti-Stokes spectra however, when rescaled by a factor of 1.64, gave approximately the same intensities as the Stokes emission spectra (both the emission spectra were recorded with the same integration times). Hence the anti-Stokes emission is approximately (10/1.66) ≈ 6 times stronger than Stokes emission.
- Error analysis: Three main possible systematic errors ought to be considered to estimate the overall error: (E1) Detector base line error for absorption, (E2) Filter transmission (E3) Error in the subtraction of a base line to determine the particle absorption in the suspension. Total error: $\Delta E = [(\Delta E_1)^2+(\Delta E_2)^2+(\Delta E_3)^2]^{0.5} = [(.110)^2+(.025)^2+(0.100)^2]^{0.5} \approx 0.15$ (=15%).

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