

# Stokes and anti-Stokes fluorescence from monoclinic $\text{Yb}^{3+}:\text{KGd}(\text{WO}_4)_2$ tungstate crystal powders synthesized by two distinct methods

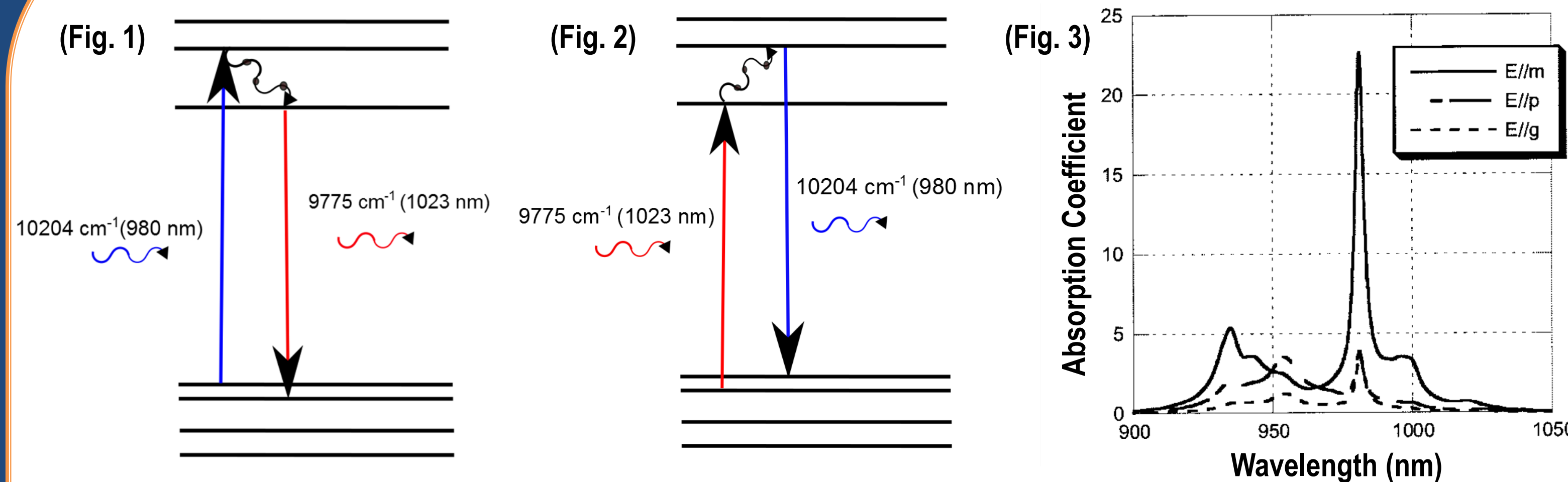
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## Introduction



(Fig. 1) Stokes fluorescence involves dissipation of photon energy into the crystal lattice. (Fig. 2) Anti-Stokes fluorescence involves annihilation of phonon energy leading to an increase in the energy of the emitted photon. (Fig. 3) Room-temperature absorption spectra in bulk  $\text{Yb}^{3+}:\text{KGd}(\text{WO}_4)_2$  for polarizations parallel to the principal refractive-index  $m$ ,  $p$ , and  $g$  axes [1].

$\text{Yb}^{3+}$  ions in a crystal lattice can produce anti-Stokes fluorescence when excited at the red edge of the absorption spectrum. Very high anti-Stokes fluorescence (ASF) yields are one of the preconditions for optical cooling of solids [2]. So far all optical cooling studies have been limited to bulk materials. Theoretical studies on ASF in nano-crystalline powders predict an enhancement of optical cooling 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 (enhanced electron number), and (iii) enhanced phonon density of states (enhanced phonon number) [3]. In this work, anti-Stokes and Stokes fluorescence spectra of  $\text{Yb}^{3+}:\text{KGd}(\text{WO}_4)_2$  powdered crystal samples prepared in two different ways are investigated.

## Experiment

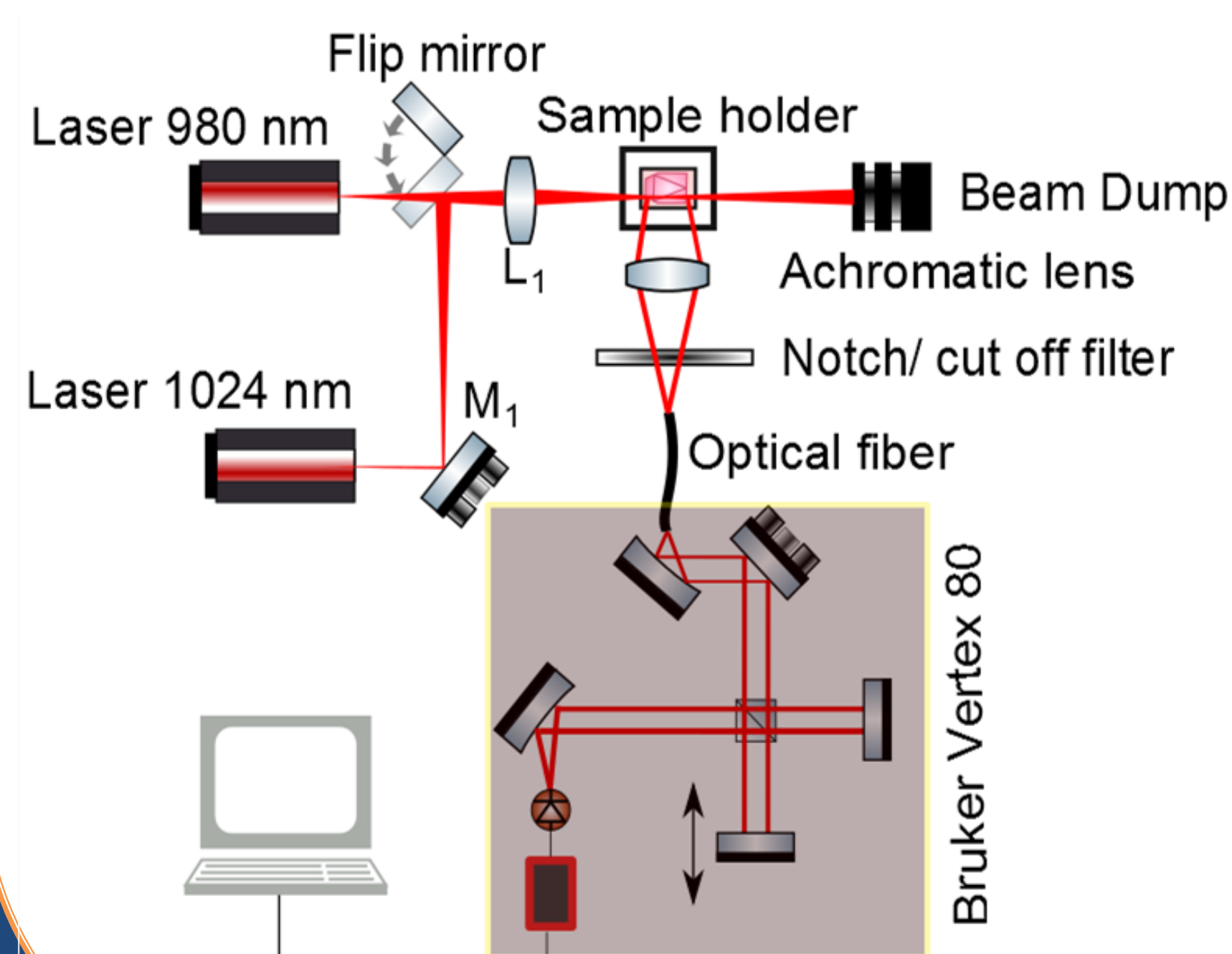
### Sample Types

Two different samples of 5%  $\text{Yb}^{3+}:\text{KGd}(\text{WO}_4)_2$  were prepared:

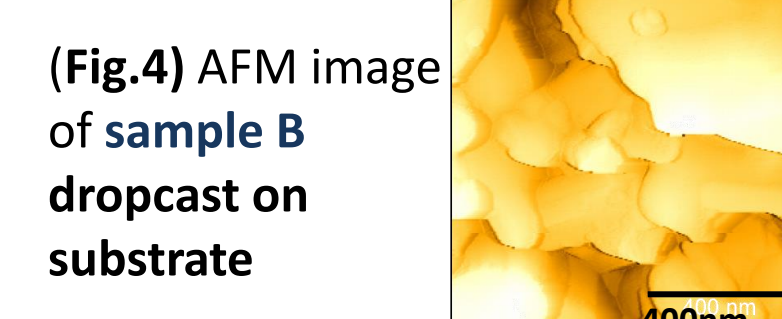
- (A) A bulk crystal using a **high temperature solution growth technique** [4] then crushed into a micro crystal powder. (**Sample A**)
- (B) Nano crystals grown by a **sol-gel modified Pechini method** [5]. (**Sample B**)

- (i) Both powders were drop cast on glass substrates. Thick coatings of around 80-100  $\mu\text{m}$  thickness were produced.
- (ii) Centrifuged suspensions of both powders in DMSO were prepared.

### Experimental set up



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  $\text{cm}^{-1}$  (980 nm) and a 20 mW laser (LD 1024 laser module, Frankfurt laser company) was used for excitation at 9775  $\text{cm}^{-1}$  (1023 nm). A flip mirror was used for convenience in choosing the source. The laser beam was grazing incidence to the coating on the substrate. For suspensions, the excitation beam was aligned close to the walls of the cuvette to ensure minimum re-absorption. 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 GmbH). The output of the fiber was coupled into a Fourier Transform spectrometer (FTS Bruker Vertex 80, maximum resolution 0.08  $\text{cm}^{-1}$ ) supplied with an InGaAs photodiode sensor. Typical fluorescence acquisition times were 90 min and 180 min for coated substrate samples and suspensions, respectively.



(Fig. 4) AFM image of sample B dropcast on substrate

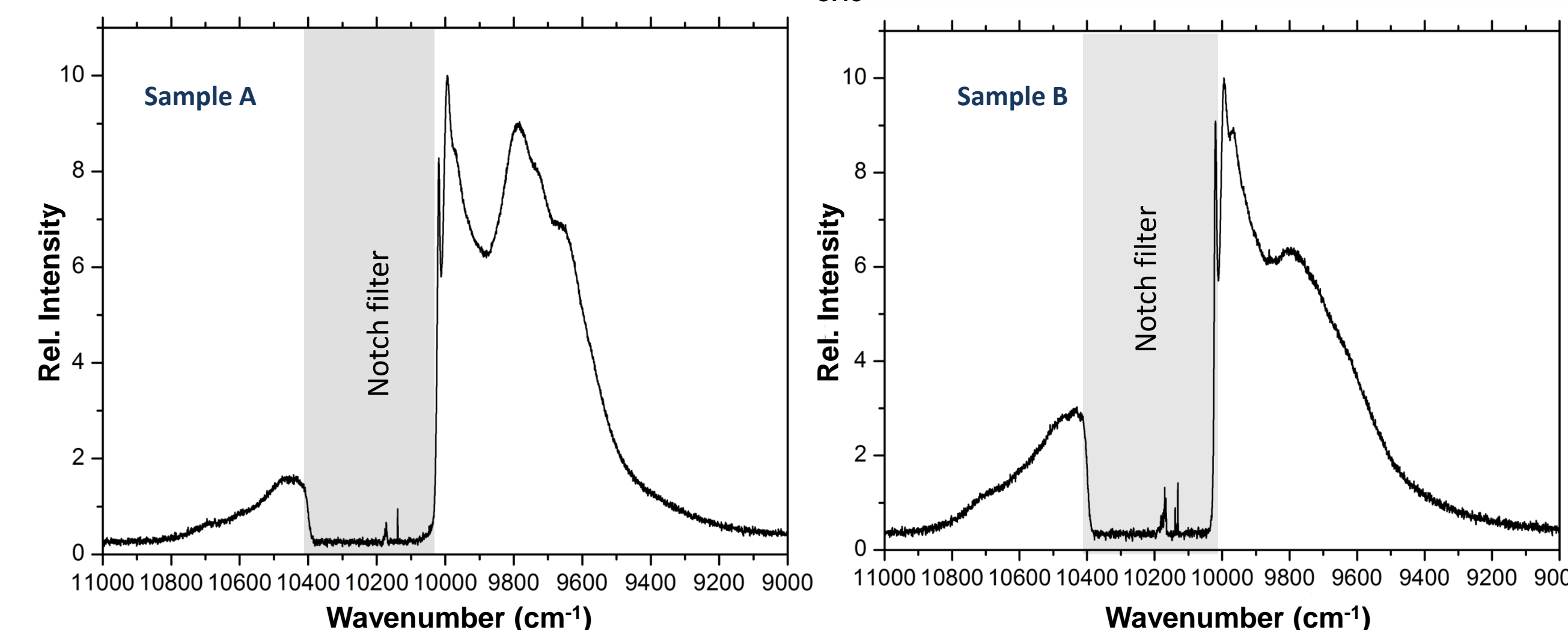
## Results

### Sample A

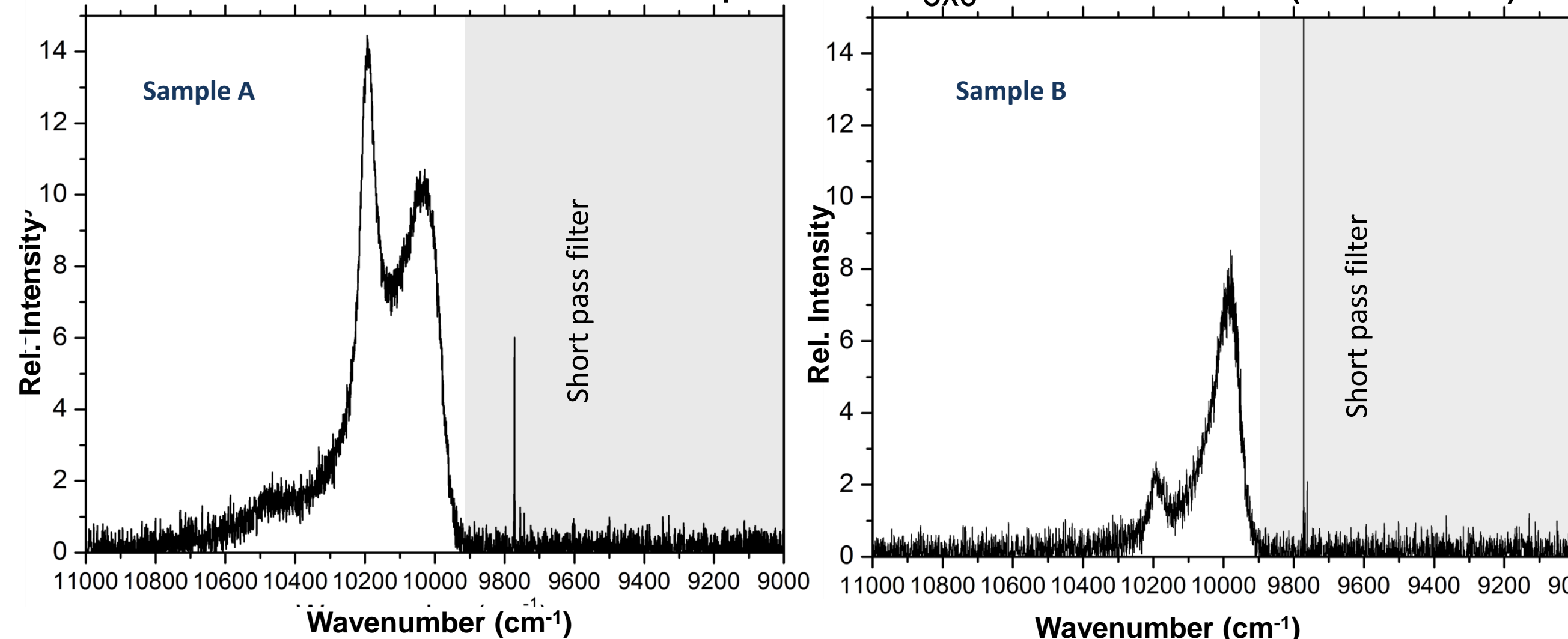
### Sample B

#### (i) Coated glass substrates

Stokes emission spectra,  $\lambda_{\text{exc}} = 10204 \text{ cm}^{-1}$  (980 nm)

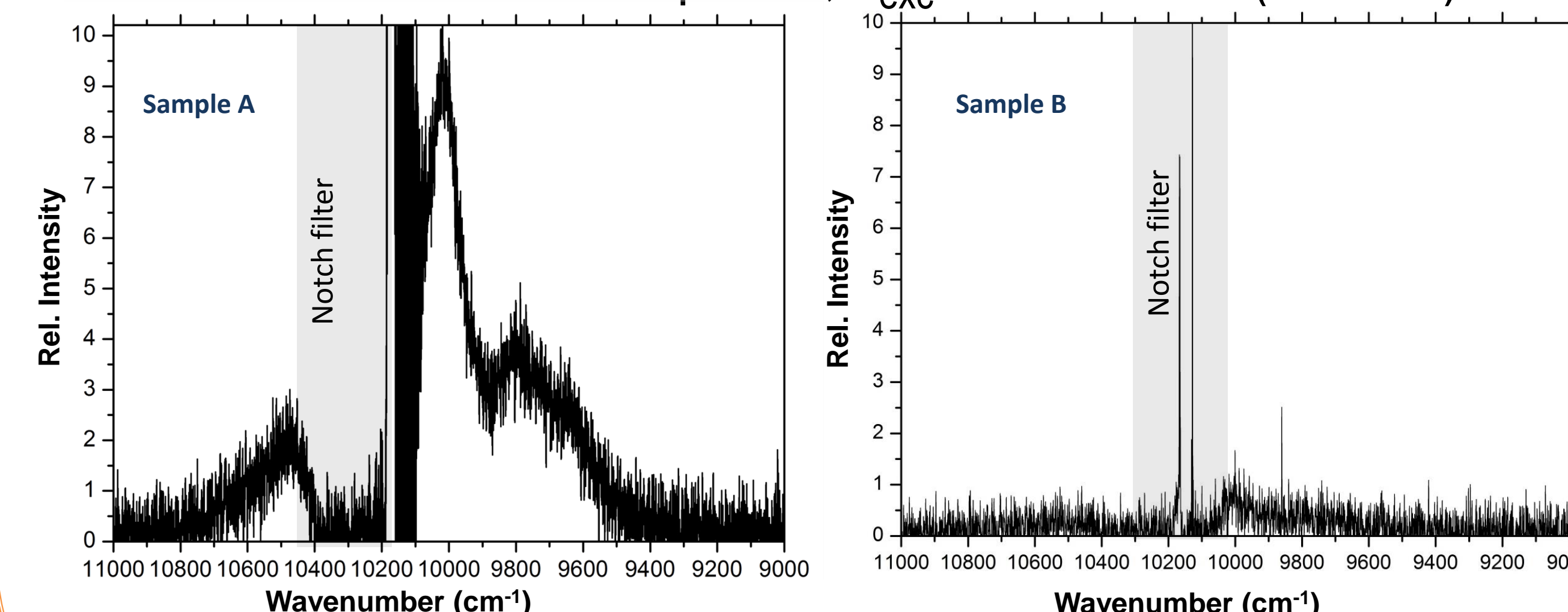


Anti-Stokes emission spectra,  $\lambda_{\text{exc}} = 9775 \text{ cm}^{-1}$  (1023 nm)



#### (ii) Dilute suspensions

Stokes emission spectra,  $\lambda_{\text{exc}} = 10204 \text{ cm}^{-1}$  (980 nm)



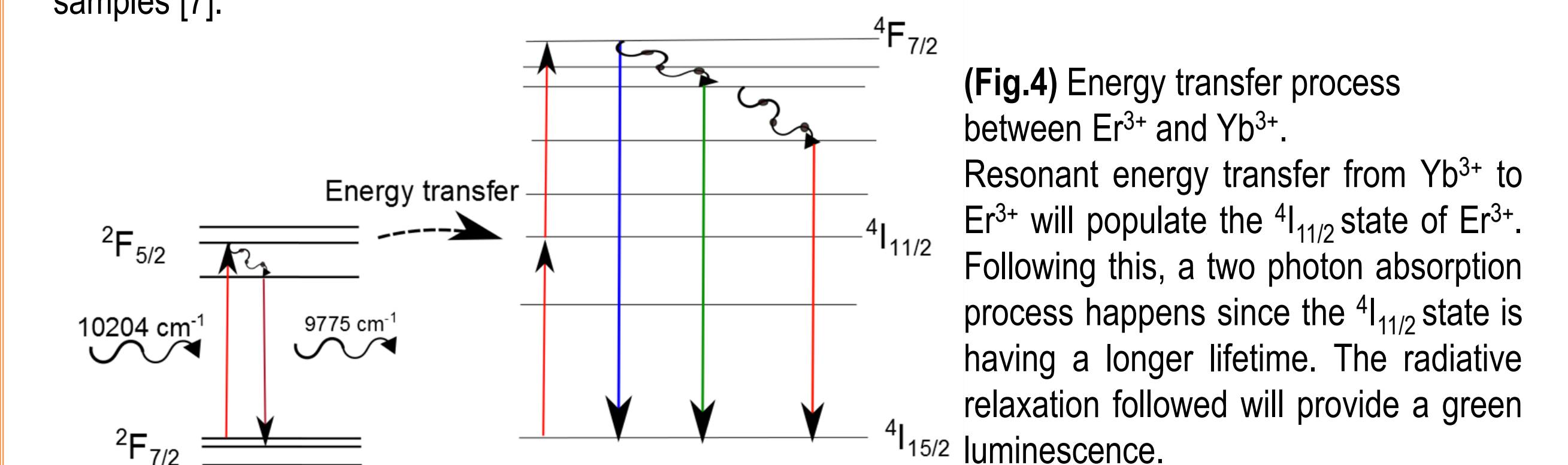
Anti-Stokes fluorescence from suspensions was extremely feeble and is therefore not shown.

## Discussion

- (i) Anti-Stokes and Stokes Fluorescence were observed from **Sample A** and **B**.
- (ii) The emission spectra of **Sample A** resembled those of the bulk crystal. Those of **Sample B** did not. The difference in the spectra has been attributed to the presence of ligands which are used in the chemical synthesis of **Sample B**.

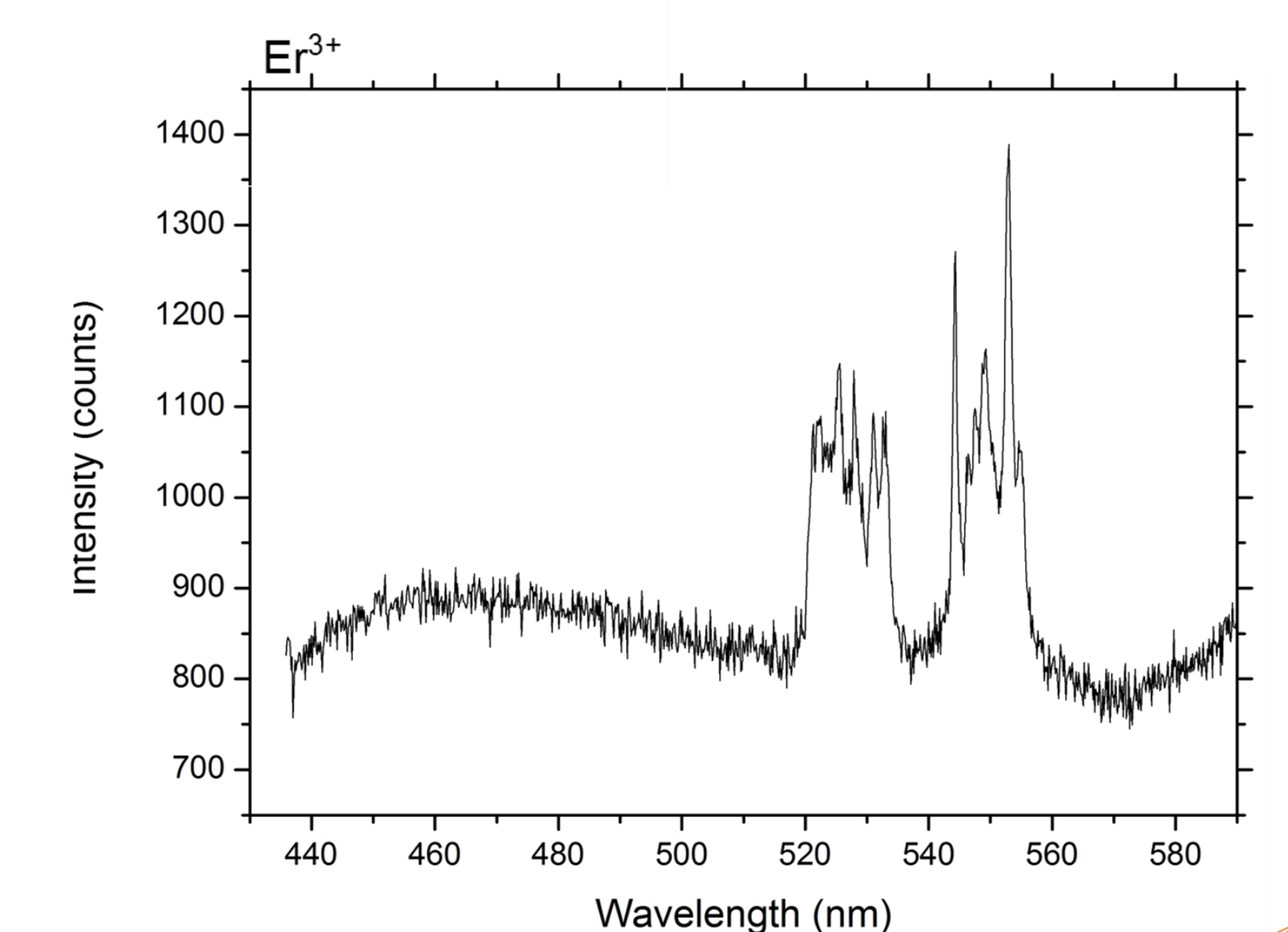
#### Fluorescence efficiencies:

- (i) The emission efficiency of all powdered samples decreased in comparison to the bulk material, due to resonant energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$ ; the latter is an inherent impurity in  $\text{Yb}^{3+}:\text{KGd}(\text{WO}_4)_2$  [6].
- (ii) In suspension, the non-radiative energy transfer to the molecular solvent environment appears to be significantly more efficient than energy transfer between  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  causing fluorescence yields (both Stokes and anti-Stokes) in suspension to be very low.
- (iii) The surface defects cause a significant drop in the overall emission efficiency of the powdered samples [7].



(Fig. 4) Energy transfer process between  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ . Resonant energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  will populate the  $^4\text{I}_{11/2}$  state of  $\text{Er}^{3+}$ . Following this, a two photon absorption process happens since the  $^4\text{I}_{11/2}$  state is having a longer lifetime. The radiative relaxation followed will provide a green luminescence.

(Fig. 5) Upconverted emission from 5%  $\text{Yb}:\text{KGW}$  bulk sample at 980 nm excitation.



## References

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