Excitation Dependent Visible and NIR Photoluminescence Properties of Er^{3+}, Yb^{3+} Co-doped $NaBi(MoO_4)_2$ Nanomaterials

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1. Experimental:

1.1 Materials

Bismuth nitrate pentahydrate (>99.9%, $Bi(NO_3)_3.5H_2O$), Sodium molybdate dihydrate (>99.9%, $Na_2MoO_4.2H_2O$), Ytterbium nitrate pentahydrate (>99.9%, $Yb(NO_3)_3.5H_2O$) were purchased from Sigma Aldrich. Erbium nitrate pentahydrate (>99.9%, $Er(NO_3)_3.5H_2O$) was bought from Alfa Aesar. Ethylene glycol ($C_2H_4O_2$, Emparta grade) was purchased from Merck Millipore, India.

1.2 Synthesis of undoped and Er^{3+}, Yb^{3+} doped $NaBi(MoO_4)_2$ nanomaterials

Yb^{3+}, Er^{3+} co-doped $NaBi(MoO_4)_2$ nanomaterials were synthesized through a simple co-precipitation method at room temperature. For the synthesis of undoped $NaBi(MoO_4)_2$ nanomaterials, 2.0615 mmol of $Bi(NO_3)_3.5H_2O$ was dissolved in 20 ml ethylene glycol by heating at 60 °C and stirring. After that, the solution was naturally cool down to room temperature. To this solution, 5 mL aqueous solution containing 8.5762 mmol of $Na_2MoO_4.2H_2O$ was added under vigorous stirring at room temperature. . Immediately, the colorless transparent solution becomes milky white and stirring was continued for 2 hours. After that, white precipitate was separated by centrifugation and then washed with ethanol, distilled water, and acetone several times and dried under ambient conditions for overnight. For the synthesis of doped samples, part of the bismuth is replaced with dopants. Amount of $Na_2MoO_4.2H_2O$ was remain constant. Amounts of $Bi(NO_3)_3.5H_2O$, $Er(NO_3)_3.5H_2O$, $Yb(NO_3)_3.5H_2O$ materials to synthesize different samples of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ nanomaterials are given in the below table TS1.

Table TS1: Amounts of precursor materials used for the synthesis of different doped nanomaterials

Compound Name	Amount of $Bi(NO_3)_3.5H_2O$ (mmol)	Amount of $Er(NO_3)_3.5H_2O$ (mmol)	Amount of $Yb(NO_3)_3.5H_2O$ (mmol)
$NaBi(MoO_4)_2$	2.0615	0	0
$NaBi_{0.89}Er_{0.01}Yb_{0.1}(MoO_4)_2$	1.8347	0.0206	0.2062
$NaBi_{0.87}Er_{0.03}Yb_{0.1}(MoO_4)_2$	1.7935	0.0618	0.2062
$NaBi_{0.85}Er_{0.05}Yb_{0.1}(MoO_4)_2$	1.7523	0.1031	0.2062
$NaBi_{0.80}Er_{0.10}Yb_{0.1}(MoO_4)_2$	1.6492	0.2062	0.2062

1.3 Characterization:

The phase composition of the synthesized nanoparticles has been determined using a Bruker D8 Advance X-ray diffractometer (Ni-filtered Cu-Kα radiation, λ = 1.5406 Å, V=40 kV, I= 25 mA). Morphology and particle size of as synthesized nanomaterials were examined using a JEOL 2100 transmission electron microscope (TEM) operated at 200 keV. UV-vis diffuse réflectance measurements were carried out in the range of 200-800 nm using Shimadzu UV-2600 spectrophotometer and $BaSO_4$ was used as reference. Fourier transform infrared (FTIR) spectra were recorded in the range of 200 - 4000 cm^{-1} with 4 cm^{-1} resolution using Bruker Vertex 70 series spectrometer with attenuated total reflectance (ATR) mode. The Raman spectra measurements were recorded using WI Tech Raman Spectrometer equipped with He-Ne laser (wavelength 633 nm, P_{min}= 35 mW, P_{max}= 50 mW, spot size 1 µm). In addition, the 45 mW laser power was focused on the samples to avoid the sample decomposition.

1.4. Photoluminescence measurements:

All luminescence properties were measured at room temperature using Fluorolog 3-221 fluorimeter. Powder samples were used to record all the photoluminescence properties. Hamamatsu R5509-73 PMT detector with C9940-02 liquid nitrogen cooler was used for NIR luminescence measurements. Hamamatsu R928 multi alkali PMT was used for all the visible

emission measurements. Powder sample holder filled with powder sample was used for measurements. For upconversion measurements, Opto Engine LLC MDL-III-980 nm CW diode laser was used as excitation source and emission slit width was kept 2 nm. The power density of the laser excitation source at the sample position was 2.75 W/cm^2. The output power of the laser was measured with Newport power meter model no 1918-R. For visible emission measurements, 450W Xenon lamp was used as excitation source. Excitation and emission slit widths are 4nm, 4nm, respectively.

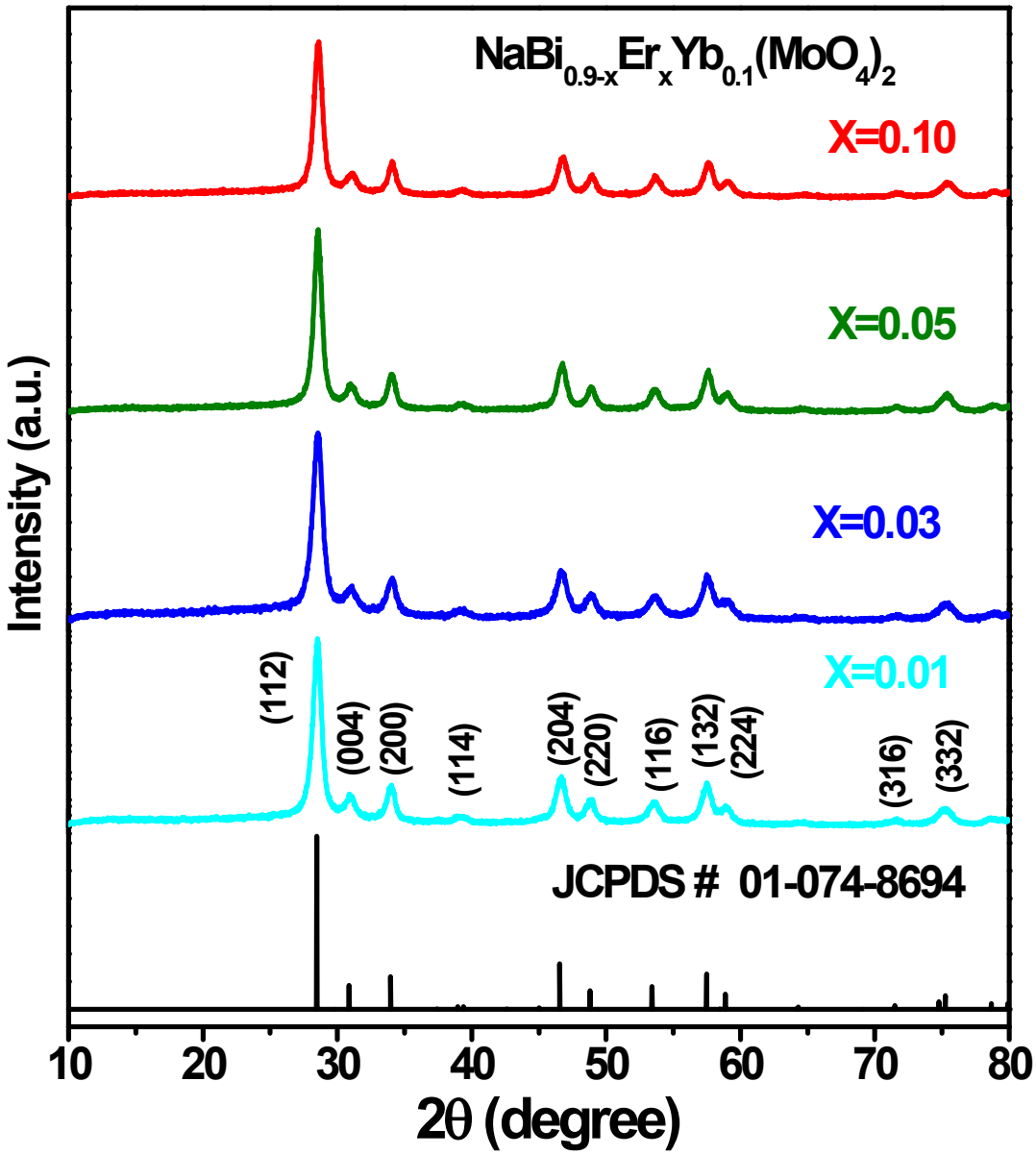

Figure S1. XRD patterns of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ ($0.01 \leq x \leq 0.10$) nanomaterials.

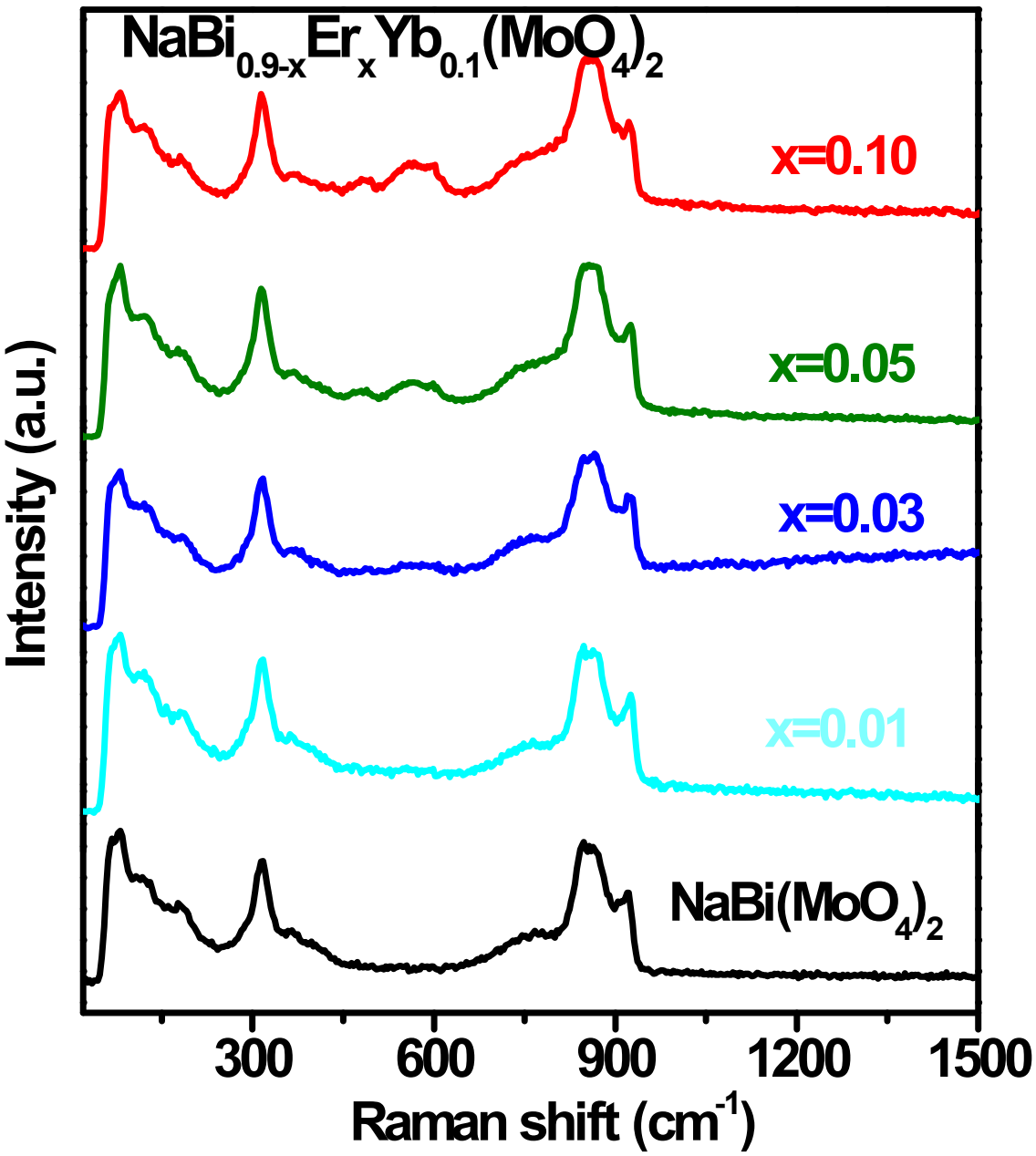

Figure S2. Raman spectra of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ ($0.01 \leq x \leq 0.10$) nanomaterials.

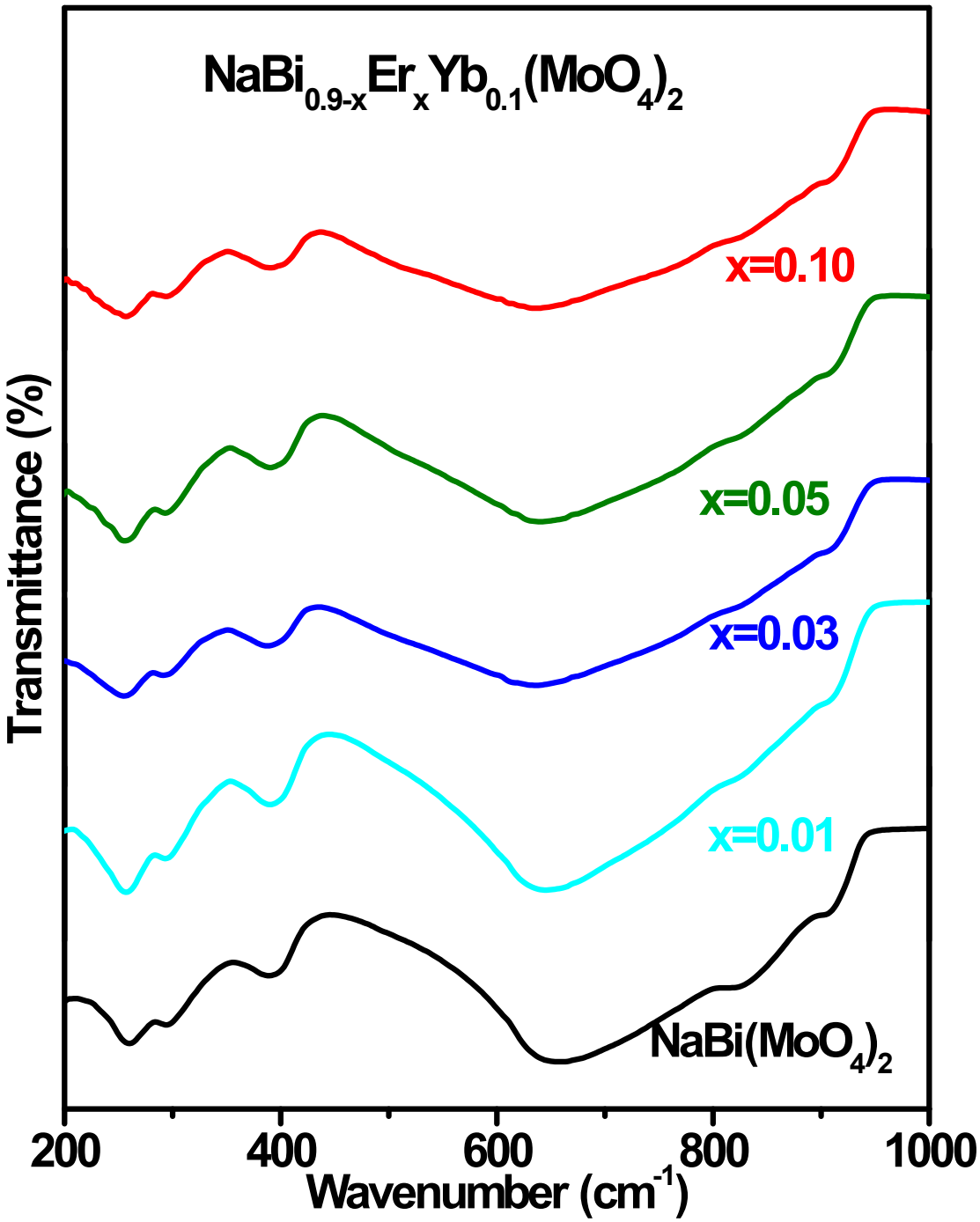

Figure S3. FTIR spectra of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ ($0.01 \leq x \leq 0.10$) nanomaterials.

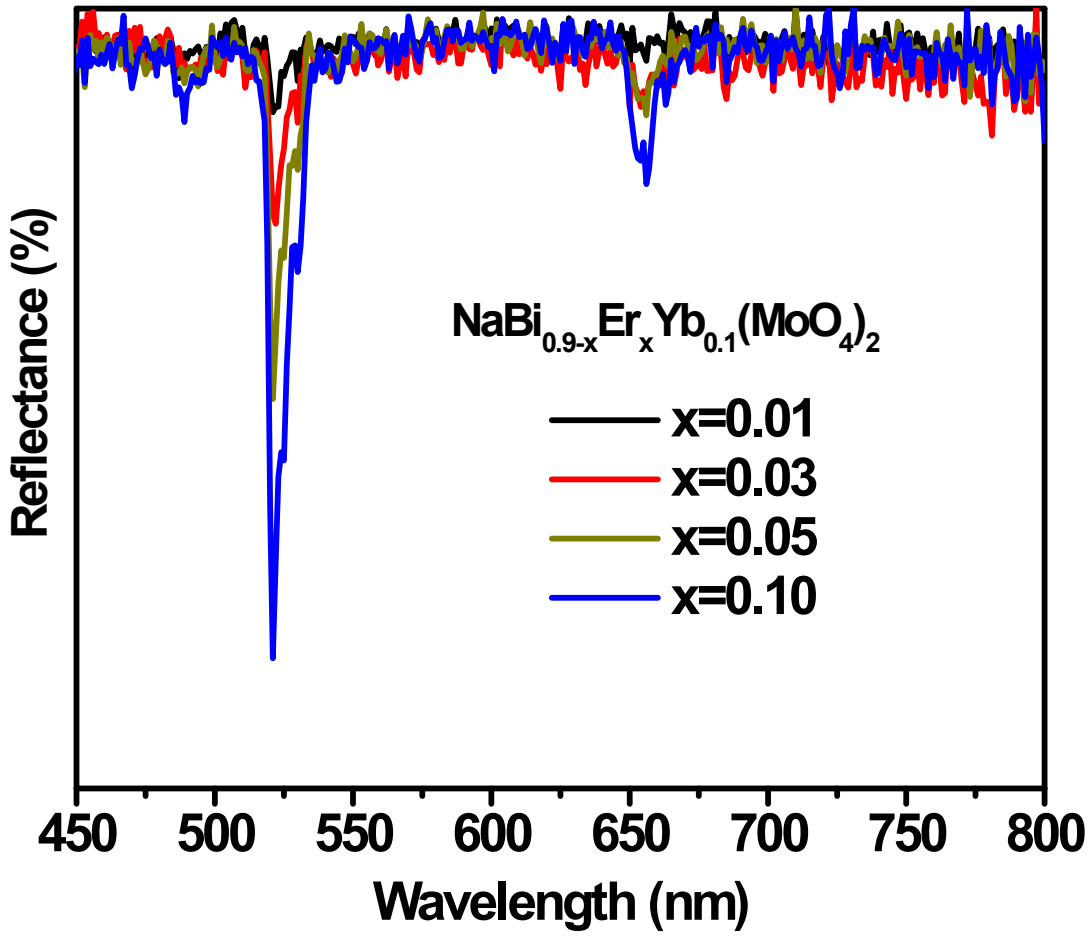

Figure S4. UV-vis diffused reflectance spectra of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ ($0.01 \leq x \leq 0.10$) nanomaterials.

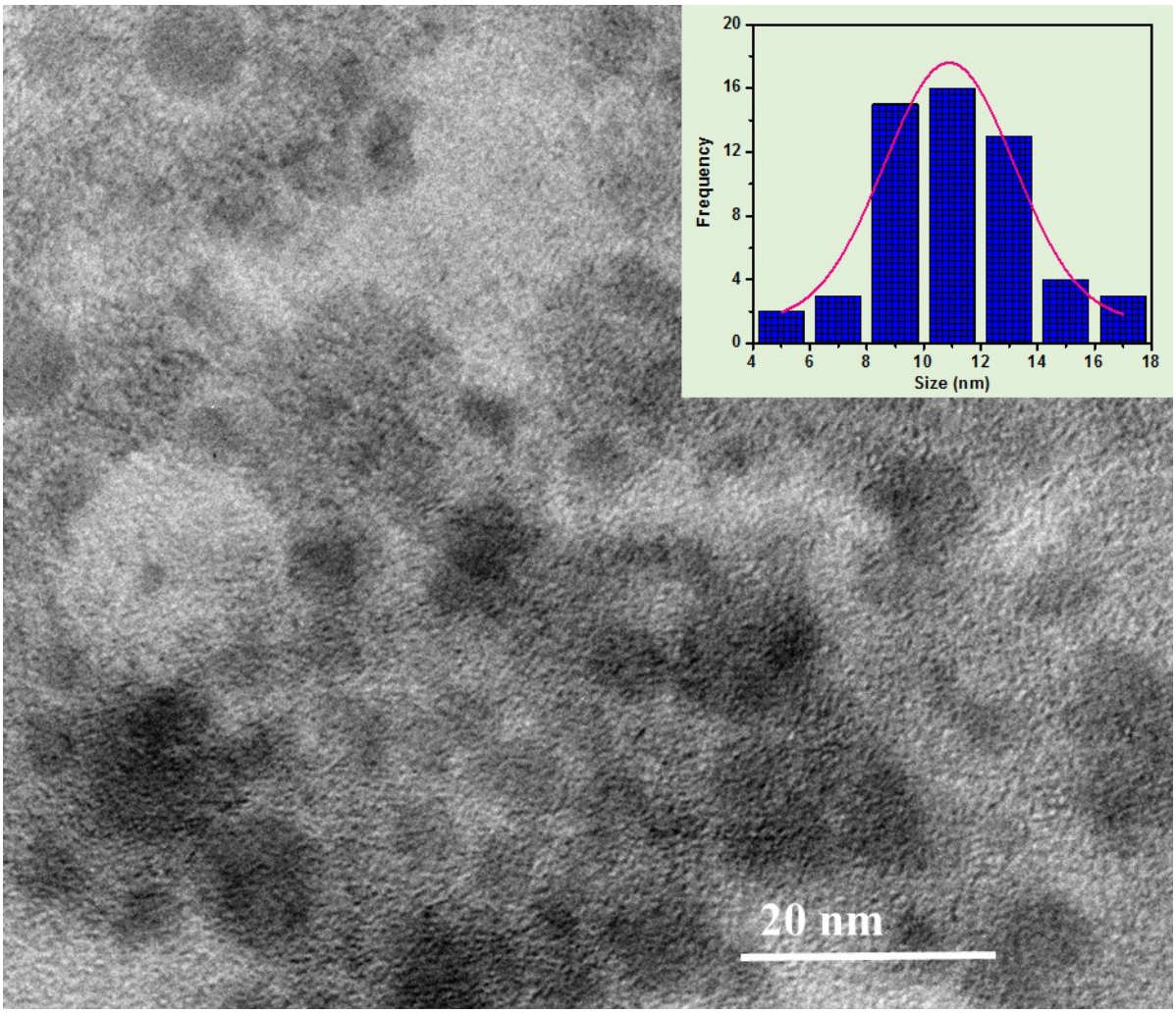

Figure S5. TEM image and particle size distribution histogram of $NaBi_{0.85}Er_{0.05}Yb_{0.1}(MoO_4)_2$nanomaterials.

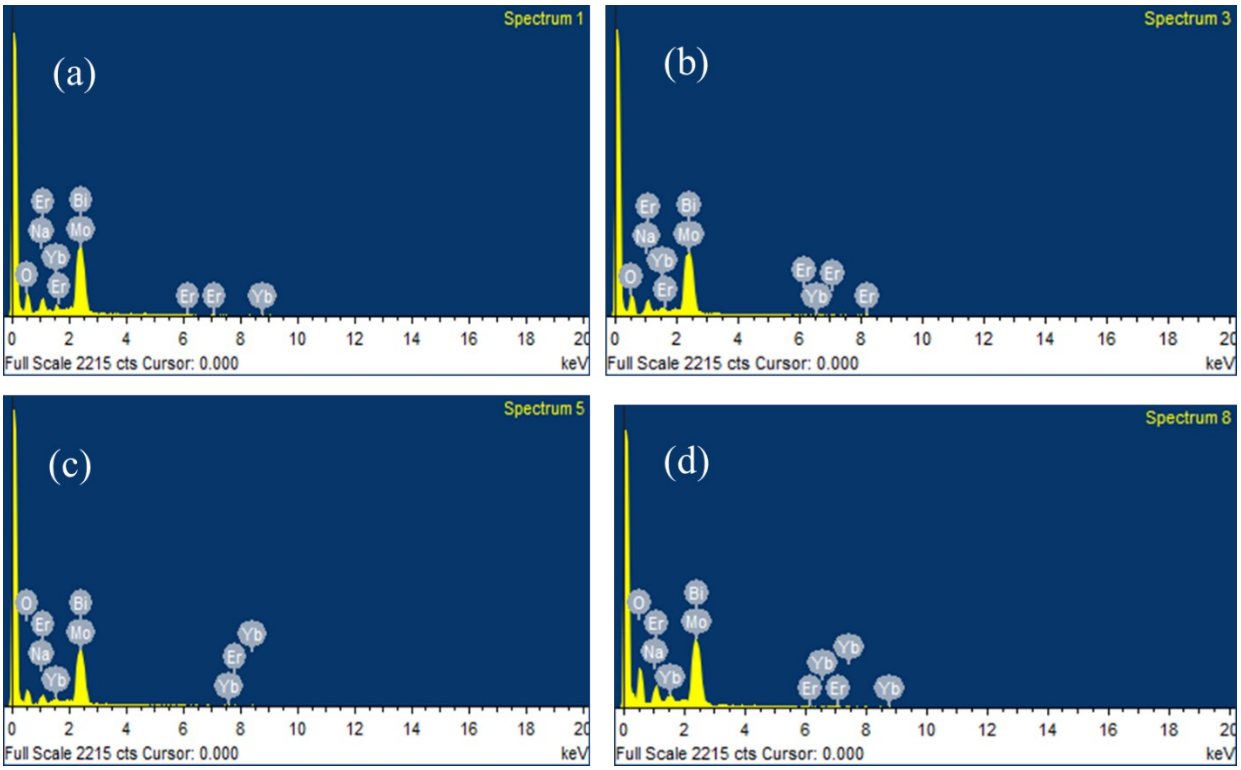

Figure S6. Energy dispersive X-ray spectra (EDS) of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ nanomaterials when (a) x=0.01, (b) x=0.03, (c) x=0.05 and (d) x=0.1.

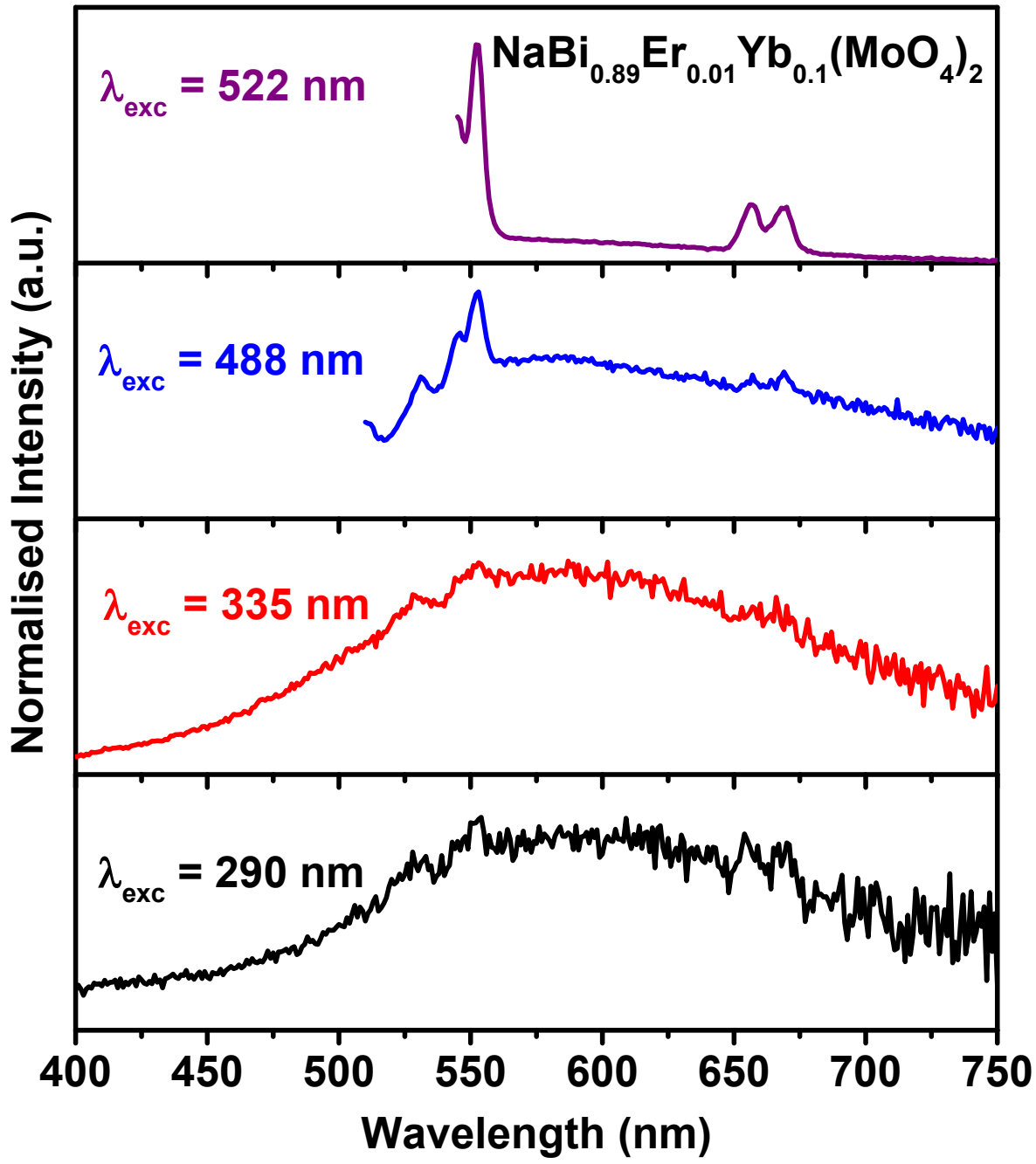

Figure S7. Photoluminescence spectra $NaBi_{0.89}Er_{0.01}Yb_{0.1}(MoO_4)_2$ nanomaterials in visible region excited at 290, 335, 452 and 522 nm.

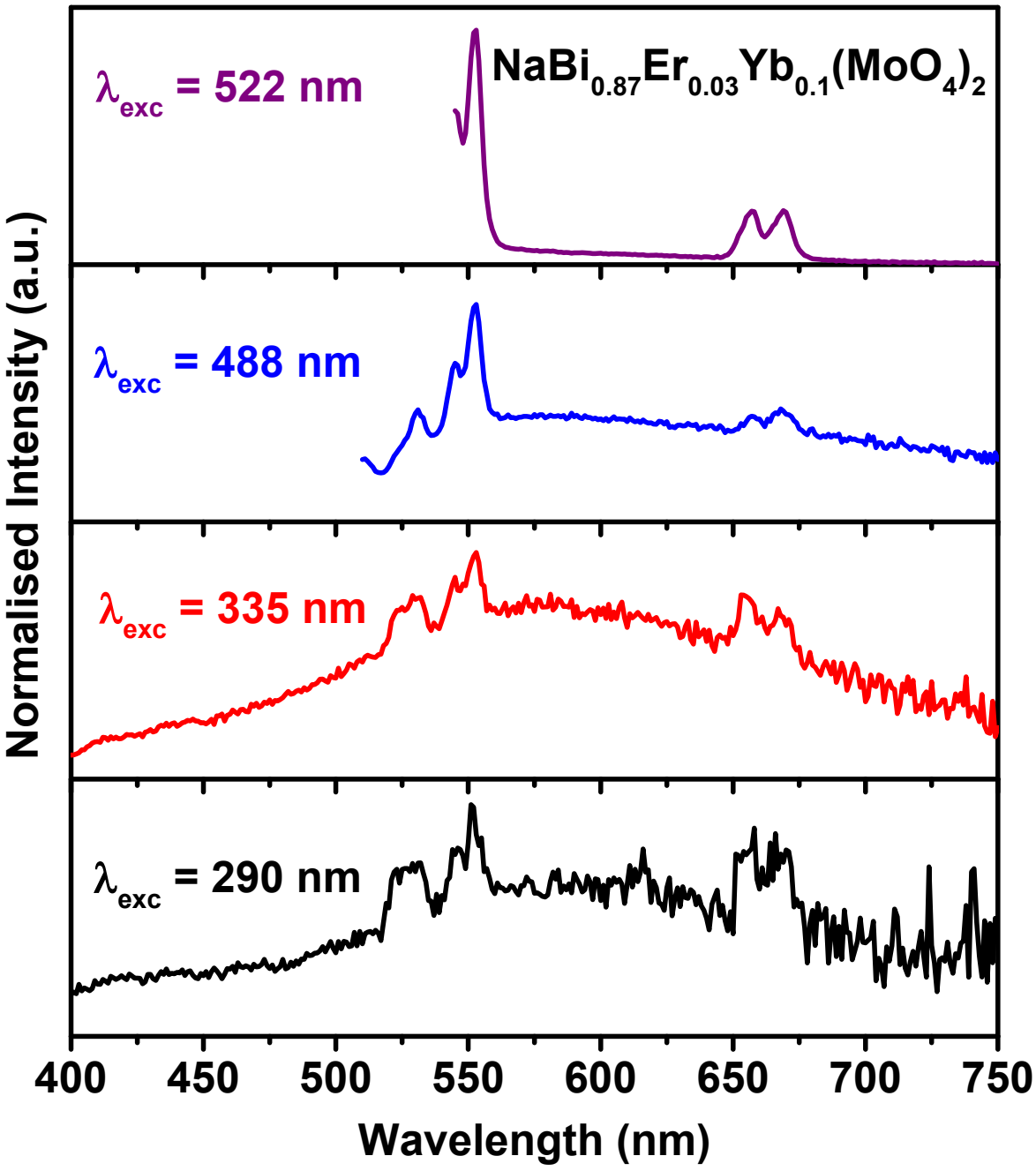

Figure S8. Photoluminescence spectra of $NaBi_{0.87}Er_{0.03}Yb_{0.1}(MoO_4)_2$ nanomaterials in visible region excited at 290, 335, 452 and 522 nm.

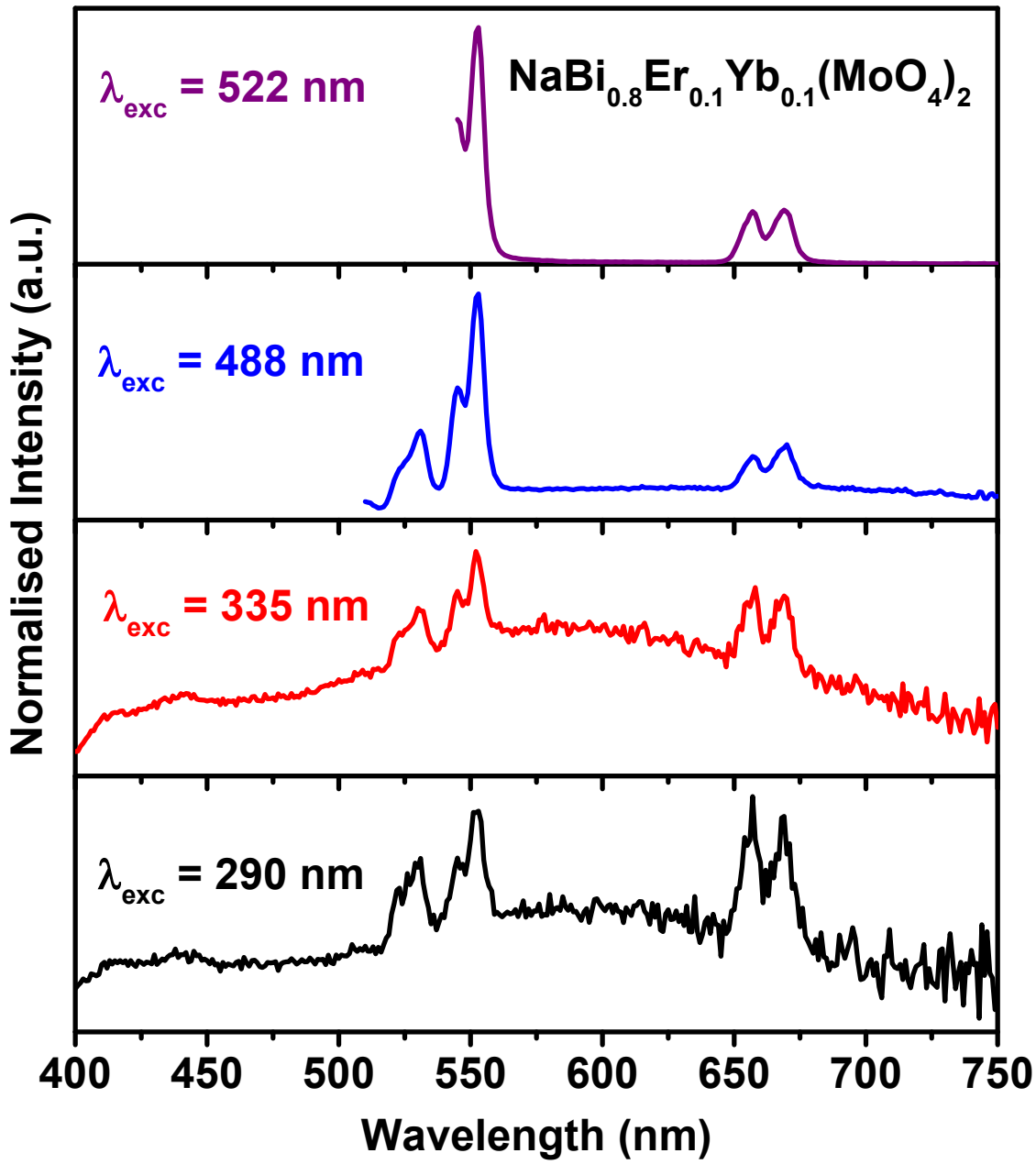

Figure S9. Photoluminescence spectra of $NaBi_{0.8}Er_{0.1}Yb_{0.1}(MoO_4)_2$ nanomaterials in visible region excited at 290, 335, 452 and 522 nm.

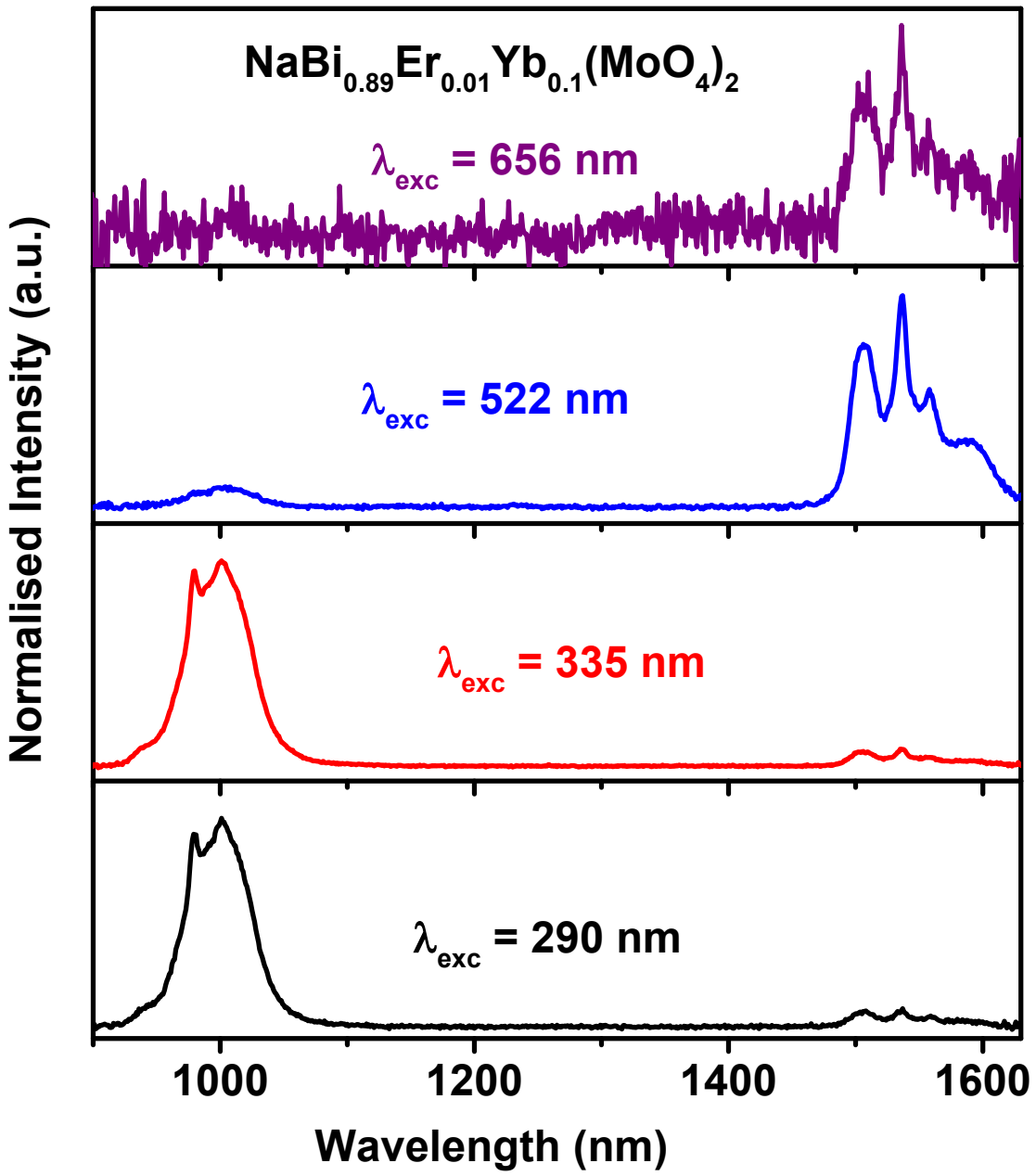

Figure S10. Photoluminescence spectra of $NaBi_{0.89}Er_{0.01}Yb_{0.1}(MoO_4)_2$ nanomaterials in NIR region excited at 335, 380, 522 and 656 nm.

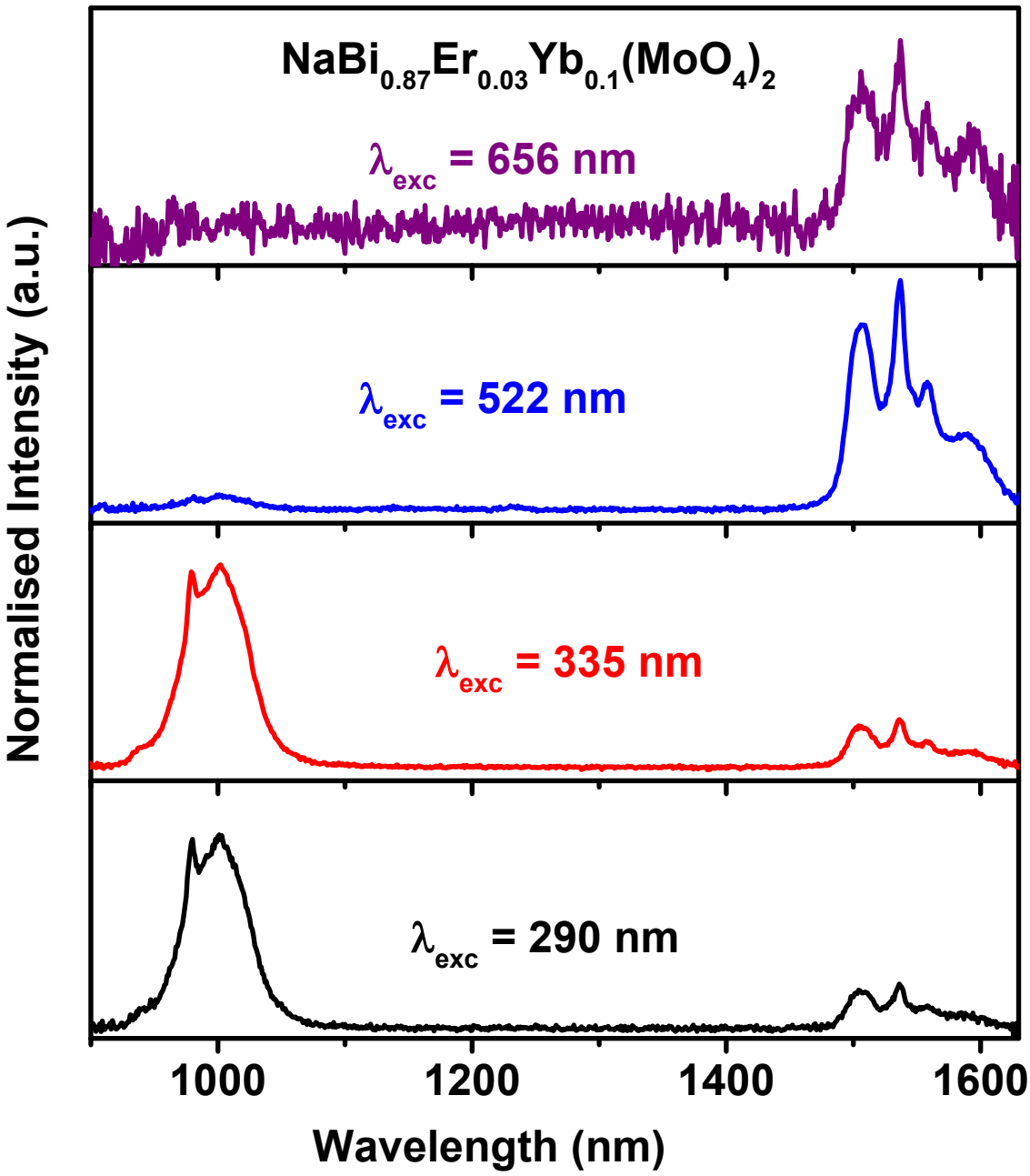

Figure S11. Photoluminescence spectra of $NaBi_{0.87}Er_{0.03}Yb_{0.1}(MoO_4)_2$ nanomaterials in NIR region excited at 335, 380, 522 and 656 nm.

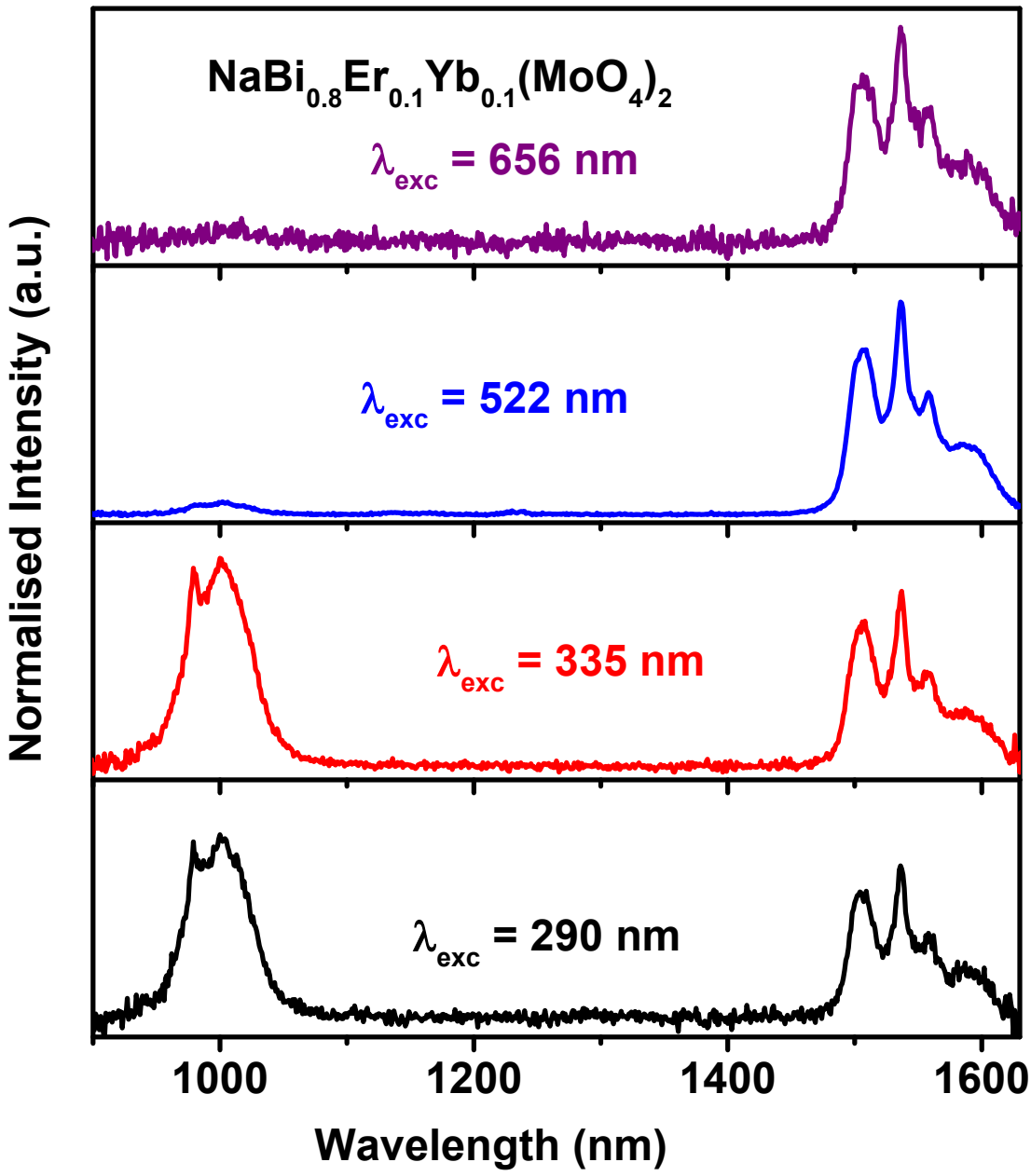

Figure S12. Photoluminescence spectra of $NaBi_{0.8}Er_{0.1}Yb_{0.1}(MoO_4)_2$ nanomaterials in NIR region excited at 335, 380, 522 and 656 nm.

Table TS2: Relative integrated intensity ratio of emission band at 1000 nm and 1534 nm of $NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$ ($0.01 \leq x \leq 0.10$) nanomaterials.

λ_{exc} (nm)	**Relative integrated intensity ratio of 1000 nm/1534 nm emission bands**			
	$NaBi_{0.9-x}Er_xYb_{0.1}(MoO_4)_2$			
	x =0.01	**x =0.03**	**x =0.05**	**x =0.10**
290	**12.01**	**4.49**	**2.52**	**1.22**
335	**11.81**	**4.31**	**2.54**	**1.21**
380	**9.86**	**3.32**	**1.68**	**0.76**
522	**0. 09**	**0.07**	**0.09**	**0.05**
656	**0.07**	**0.06**	**0.06**	**0.07**