

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Information for
**Downshifting in Cs₂NaBiCl₆:Er³⁺: transforming ultraviolet into near
infrared radiation**

Anjun Huang,^a Chang-Kui Duan,^b Ka-Leung Wong ^{*a} and Peter A. Tanner ^{*a}

^a Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon Tong, Hong Kong, China.

^b CAS Key Laboratory of Microscale Magnetic Resonance, University of Science and Technology of China, Hefei 230026, China.

Contents

Item	Title	Page S
S1	Syntheses	2
S2	Instrumental measurements	3
Fig. S1	(a) Detail of Figure 2a: 520 nm xenon lamp excited emission spectrum at room temperature (black) and 77 K (red) spectra of Cs ₂ NaBi _{0.95} Er _{0.05} Cl ₆ recorded by the Fluorolog-3 Instrument. (b) Room temperature emission spectrum excited by Nd-YAG pulsed laser excited optical parametric oscillator at 520 nm of Cs ₂ NaBi _{1-x} Er _x Cl ₆ (x = 0, 0.01, 0.05) and recorded by the iHR550 detector.	4
Fig. S2	(a) Temperature dependent emission spectra of Cs ₂ NaBi _{0.95} Er _{0.05} Cl ₆ micron-sized powder sample under 375 nm excitation; (b) the plot of temperature and integrated peak area ratio of the emission band centred at 960 nm and the peak at 1542 nm. The red line is the fit given by the equation.	4
S3	Notes and references	5

S1. Syntheses

Bismuth (III) acetate (99.999%), cesium acetate (99.998%), cesium chloride (99.999%), sodium acetate (99.997%), sodium carbonate (99.99%), erbium (III) chloride hydrate (99.99%), diphenyl ether (DPE, 99%) and benzoyl chloride (Bz-Cl, 99+%) were purchased from Alfa Aesar. Erbium(III) acetate tetrahydrate (99.9%) was from Strem, and bismuth (III) oxide (99.9%) was from Across. Oleic acid (OA, 90%), oleylamine (OLA, 90%), ethyl acetate (99.8%), and hexane (97%) were purchased from Energy. Hydrochloric acid (37%) was purchased from RCI Labscan. Toluene (99.5%) was from Duksan Pure Chemicals. None of the above chemicals were further purified.

The preparation of elpasolite bulk samples. The precipitation method¹ was employed to prepare $\text{Cs}_2\text{NaEr}_x\text{Bi}_{1-x}\text{Cl}_6$ ($x = 0, 0.01, 0.05$) bulk samples in concentrated HCl. In a typical synthesis process, 1 mmol Na_2CO_3 , $(1-x)$ mmol Bi_2O_3 and $2x$ mmol $\text{ErCl}_3 \cdot n\text{H}_2\text{O}$ were added into 15 mL of concentrated HCl in a round-bottomed flask and heated to 80 °C in a mantle-heater to fully dissolve the contents. Then 2 mL of CsCl solution (2 mol L^{-1}) in concentrated HCl were added, leading to the formation of a white precipitate immediately. The mixtures were kept stirred for 20 min at this temperature to ensure the complete reaction. The reaction system was then cooled down to room temperature and centrifuged at 6500 rpm for 10 min to obtain the products. The precipitates were dried at 75 °C overnight and then reheated to 165 °C for 8 h. The powders were cooled down to room temperature in the oven to give the final products.

The synthesis of elpasolite nanoparticles. The hot injection method² was used to prepare $\text{Cs}_2\text{NaEr}_x\text{Bi}_{1-x}\text{Cl}_6$ ($x = 0, 0.01, 0.05$) NPs. In a typical synthesis process, all solid raw materials were put into two-neck round-bottomed flask in the stoichiometric ratio, and 4 mL DPE, 1.2 mL OA and 0.6 mL OA were added. The mixtures were degassed at 40 °C for 50 min with stirring, and then nitrogen was filled into the system. The reactant vessel was slowly heated to 140 °C, and then a mixture of 200 μL Bz-Cl and 0.5 mL degassed DPE was quickly injected into the reaction system with vigorous stirring when the temperature reached the target temperature of 165 °C. After 10 s, the flask was put into an ice-water bath for rapid cooling.

Then reaction stock solution was centrifuged at 11000 rpm for 15 min to obtain a light gray precipitate and a brown supernatant. The precipitates were dispersed in 3 mL of hexane, and then 3 mL ethyl acetate was added. Subsequently, the mixtures were centrifuged again at 11000 rpm for 15 min. The precipitates were dispersed again in 3 mL of hexane and were centrifuged at 4500

rpm for 5 min to remove large particles. The precipitate was discarded, and the supernatant was retained as the final nano products. Then, 200 μ L stock supernatant was dispersed in 3 mL hexane or toluene to investigate local field effect. The remaining supernatant was dried in vacuum and then stored in a glass bottle with N₂ protection for further low temperature spectral measurements. The oleic acid surface chain produced by the hot injection method affords some protection for deliquescent Cs₂NaErCl₆.

S2. Instrumental measurements

The X-ray diffraction (XRD) patterns for bulk and nano samples were collected by a Bruker AXS D8 Advance X-ray diffractometer at 40 kV and 40 mA with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were recorded by a JEOL Model JEM-2100F Transmission Electron Microscope. Photoluminescence spectra at room and lower temperatures were recorded by a Horiba Fluorolog-3 spectrophotometer with a 450 W xenon lamp as light source. More clearly-resolved spectra used a Horiba iHR550 spectrometer using a Nd-YAG laser as light source (pulse duration 8 ns, repetition frequency 10 Hz, 120 mJ) with an optical parametric oscillator (OPO, Spectra-Physics versaScan and UVScan). The samples were housed in NMR quartz tubes (5 mm, Wilmad) for the room temperature and 77 K measurements, using a custom-made liquid nitrogen cryostat for the latter. A CS202-DMX-1AL closed-cycle cryostat from Advanced Research Systems (DE-202 series) was employed to house the samples in the range from 30 K to 450 K.

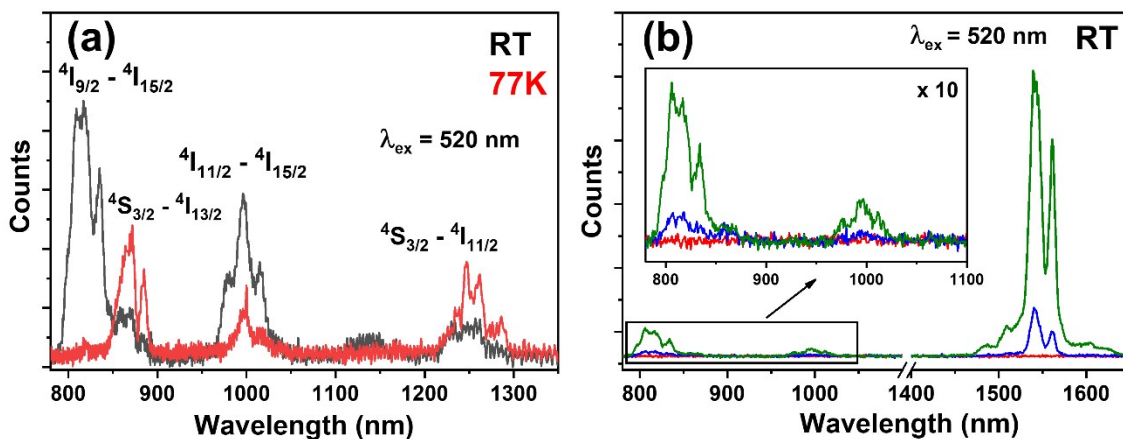


Fig. S1 (a) Detail of Figure 2a: 520 nm xenon lamp excited emission spectrum at room temperature (black) and 77 K (red) spectra of $\text{Cs}_2\text{NaBi}_{0.95}\text{Er}_{0.05}\text{Cl}_6$ recorded by the Fluorolog-3 Instrument. (b) Nd-YAG pulsed laser excited optical parametric oscillator at 520 nm emission spectrum at room temperature of $\text{Cs}_2\text{NaBi}_{1-x}\text{Er}_x\text{Cl}_6$ ($x = 0, 0.01, 0.05$) recorded by the iHR550 detector.

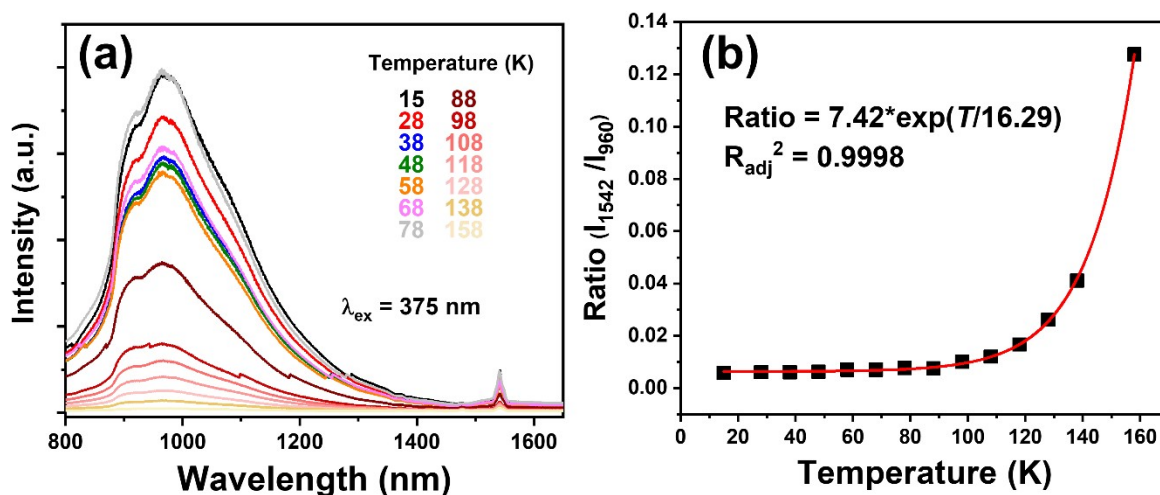


Fig. S2 (a) Temperature dependent emission spectra of $\text{Cs}_2\text{NaBi}_{0.95}\text{Er}_{0.05}\text{Cl}_6$ micron-sized powder sample under 375 nm excitation; (b) the plot of temperature and integrated peak area ratio of the emission band centred at 960 nm and the peak at 1542 nm. The red line is the fit given by the equation.

S3 Notes and references

- 1 J. D. Majher, M. B. Gray, T. A. Strom and P. M. Woodward, *Chem. Mater.*, 2019, **31**, 1738-1744.
- 2 F. Locardi, M. Cirignano, D. Baranov, Z. Dang, M. Prato, F. Drago, M. Ferretti, V. Pinchetti, M. Fanciulli, S. Brovelli, L. De Trizio and L. Manna, *J. Am. Chem. Soc.*, 2018, **140**, 12989-12995.