Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Highly efficient NIR to NIR and VIS upconversion in Er^{3+} and Yb^{3+} doped in M_2O_2S (M=Gd, La, Y)

M. Pokhrel[1], GA. Kumar[1], and D. Sardar[1]*

[1]Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX 78249

ESI S1. Synthesis and Characterization of NaYF4:20% Yb/2% Er

For comparison between the hosts, 3±1 μm sized β-$NaYF_4$ phosphor powder doped with 20% Yb^{3+}/2% Er^{3+} was synthesized using method as described in reference, which is generally accepted to give the highest quality β-$NaYF_4$: 20% Yb^{3+} /2% Er^{3+} with most efficient UC emission.[1] Fig. S1 (a) shows the scanning transmission electron microscopy (STEM) image of the β-$NaYF_4$: 20% Yb^{3+} /2% Er^{3+} phosphor. STEM image as shown in Fig. S1 (a) confirms non-uniform morphology of the particles with an average size of 3 ± 1 μm. The compositional distributions of each element in the particles were confirmed by Energy Dispersive X-ray (EDX) line and spectral mapping analysis as shown in Fig. S1 and Fig. S2. Spectral mapping was performed in a cluster of particles as shown Fig. S1 (b). Line scan spectrum was recorded through the center of a nanoparticle marked by a yellow line as shown in inset of Fig. S1 (a). EDX signals obtained from K, L, and M shell electrons were clearly traced across the region of the nanoparticles as shown in Fig. S1(c) and Fig. S1(d), which guarantees the doping of Yb^{3+}/Er^{3+}. The X-Ray, morphological characterizations, and optical properties of β-$NaYF_4$: 20% Yb^{3+}/2% Er^{3+} were compared with the reference too. [1]

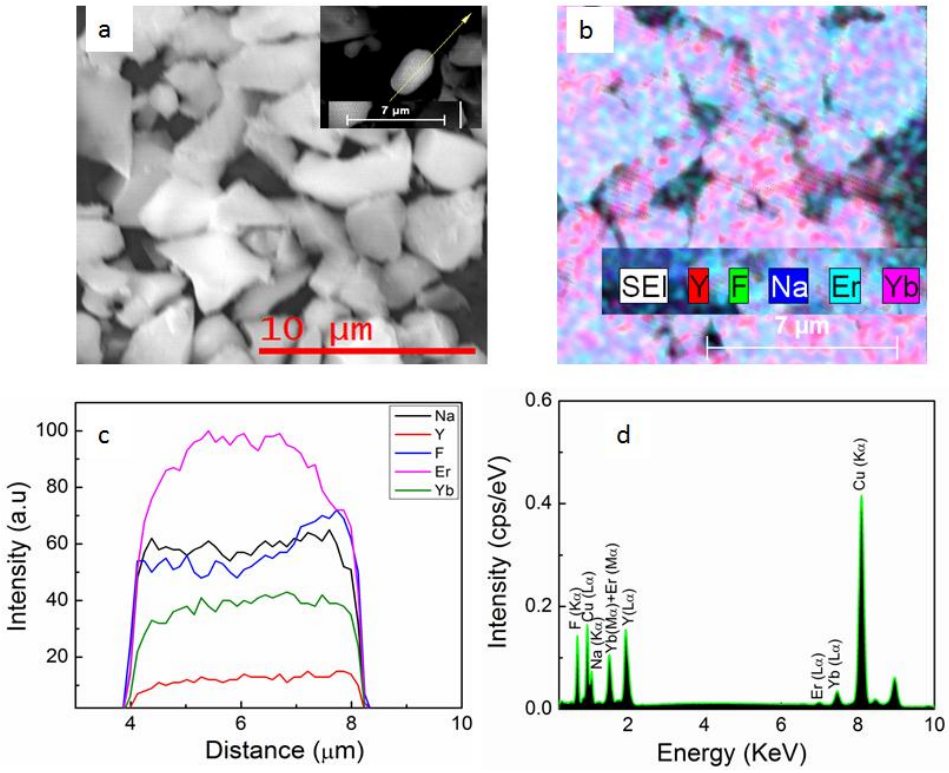

Figure S2. (a) SEM image of the $NaYF_4$: 20 % Yb^{3+}/ 2% Er^{3+} phosphor synthesized through solid state reaction, inset of 1(a) shows the EDX line scan setup for $NaYF_4$: 20 % Yb^{3+}/ 2% Er^{3+} particles (b) shows the EDX mapping scan of $NaYF_4$: 20 % Yb^{3+}/ 2% Er^{3+} particles (c) EDX line scan spectrum confirming the doping of Er^{3+} and Yb^{3+}, (d) EDX spectrum confirming the doping of Yb^{3+}/Er^{3+} into $NaYF_4$ lattice matrix

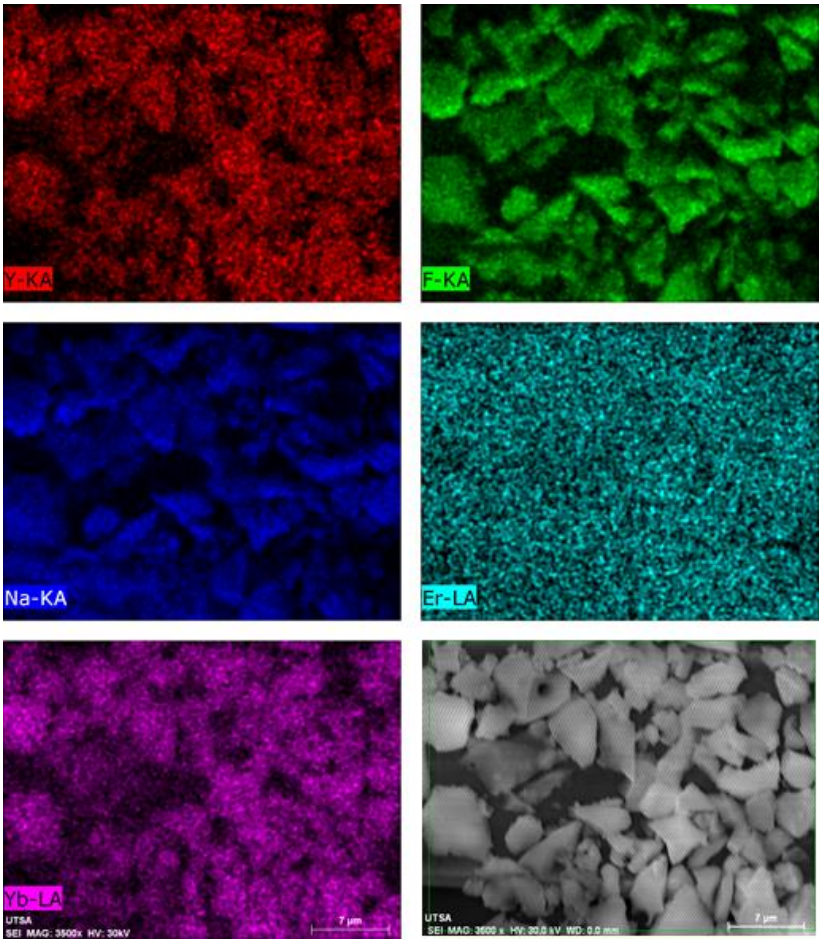

Figure S3. EDX mapping of $NaYF_4$: 20 % Yb^{3+}/ 2% Er^{3+} particles confirming the doping of Er^{3+} and Yb^{3+}

Upconversion Quantum Yield: $La_2O_2S:Yb^{3+}/Er^{3+}$

Table S4 Absolute UC QYs for different concentration of La_2O_2S: Yb^{3+}/Er^{3+}compared to that of β-$NaYF_4$:20%Yb^{3+}/2% Er^{3+} at the excitation power density of 0.5± 0.07 W/cm^2

QY at 0.5 W/cm^2(%)	UV (410 nm)	Green (550 nm)	Red (667 nm)	NIR (822 nm)	Total (QY)%
20 % Yb, 2% Er: $NaYF_4$	≈ 0	0.030±0.005	0.025±0.003	0.16±0.0.03	0.21±0.03
9%Yb, 1% Er:La_2O_2S	0.0014±0.0002	0.062±0.009	0.21±0.03	0.13±0.02	0.40±0.06
3%Yb, 7% Er:La_2O_2S	0.0014±0.0002	0.084±0.001	0.32±0.03	0.29±0.02	0.70±0.10
5%Yb, 5% Er:La_2O_2S	0.0013±0.0002	0.076±0.009	0.19±0.03	0.19±0.03	0.46±0.07
1%Yb,1%Er:La2O2S	0.0008±0.0001	0.047±0.007	0.095±0.01	0.19±0.03	0.33±0.05
1%Yb, 9% Er:La2O2S	0.0007±0.0001	0.036±0.005	0.12±0.018	0.29±0.044	0.45±0.07

Table S5 Absolute UC QYs for different concentration of La_2O_2S: Yb^{3+}/Er^{3+} compared to that of β-$NaYF_4$:20%Yb^{3+}/2% Er^{3+} at the excitation power density of 3.8 ± 0.57 W/cm^2

QY at 3.8 W/cm^2(%)	UV (410 nm)	Green (550 nm)	Red (667 nm)	NIR (822 nm)	Total (QY)%
20 % Yb, 2% Er: $NaYF_4$	0.014±0.002	0.37±0.06	0.43±0.06	0.86±0.13	1.67±0.25
9%Yb, 1% Er:La_2O_2S	0.020±0.003	0.69±0.10	3.13±0.50	1.03±0.15	4.87±0.73
3%Yb, 7% Er:La_2O_2S	0.015±0.002	0.56±0.10	1.62±0.24	2.53±0.40	4.72±0.72
5%Yb, 5% Er:La_2O_2S	0.015±0.002	0.67±0.10	1.88±0.3	1.51±0.20	4.07±0.6
1%Yb,1%Er:La2O2S	0.0018±0.0003	0.17±0.03	0.38±0.05	0.29±0.04	0.84±0.12
1%Yb, 9% Er:La2O2S	0.0052±0.0008	0.24±0.036	0.81±0.12	1.35±0.20	2.41±0.36

Table S6. Absolute UC QY for La_2O_2S: 9% Yb^{3+} /1% Er^{3+} compared to that of $NaYF_4$: 20% Yb, 2% Er at their threshold excitation power densities and at 3.8 ± 0.57 W/cm^2

QY (%)	UV (410 nm)	Green (550 nm)	Red (667 nm)	NIR (822 nm)	Total (QY)%
20 % Yb, 2% Er: $NaYF_4$ at 22 W/cm^2	0.11±0.02	1.66±0.20	2.5±0.40	3.53±0.50	7.8±1.2
9%Yb, 1% Er:La_2O_2S at 22 W/cm^2	0.0047±0.0004	0.57±0.08	1.59±0.23	0.50±0.07	2.66±0.4
20 % Yb, 2% Er: $NaYF_4$ at 13 W/cm^2	0.072±0.001	1.07±0.16	1.6±0.24	2.2±0.33	4.9 ± 0.7
9%Yb, 1% Er:La_2O_2S at 13 W/cm^2	0.024±0.004	0.87±0.10	3.84±0.60	1.1±0.16	5.83±0.8
20% Yb,2% Er: $NaYF_4$ at 3.8 W/cm^2	0.014±0.002	0.37±0.05	0.43±0.06	0.86±0.13	1.67±0.3
9%Yb, 1% Er:La_2O_2S at 3.8 W/cm^2	0.020±0.003	0.69±0.10	3.13±0.50	1.03±0.15	4.87± 0.7

Upconversion Quantum Yield: $Y_2O_2S:Yb^{3+}/Er^{3+}$

Table S7 Absolute UC QY for different concentrations of Y_2O_2S: Yb^{3+}/ Er^{3+} at the excitation power density of 3.8 ± 0.57 W/cm^2

QY at 3.8 W/cm^2(%)	UV (410 nm)	Green (550 nm)	Red (667 nm)	NIR (822 nm)	Total (QY)%
2%Yb, 8% Er:Y_2O_2S	0.001±0.0001	0.094±0.015	0.21±0.10	0.86±0.12	1.2±0.17
3%Yb, 7% Er:Y_2O_2S	0.0065±0.001	0.15±0.023	0.35±0.05	0.76±0.11	1.26±0.20
5%Yb, 5% Er:Y_2O_2S	0.0054±0.0008	0.16±0.023	0.41±0.06	0.53±0.10	1.10±0.16
0%Yb, 1% Er:Y_2O_2S	0.0032±0.0005	0.087±0.015	0.33±0.05	0.78±0.11	1.20±0.18
1%Yb, 1% Er:Y_2O_2S	0.0034±0.0005	0.090±0.015	0.12±0.021	0.91±0.13	1.12±0.16

Upconversion Quantum Yield: $Gd_2O_2S:Yb^{3+}/Er^{3+}$

Table S8 Absolute UC QY for different concentrations of Gd_2O_2S: Yb^{3+}/Er^{3+} at the excitation power density of 0.5 ± 0.07 W/cm2

QY at 0.5 W/cm²(%)	UV (410 nm)	Green (550 nm)	Red (667 nm)	NIR (822 nm)	Total (QY)%
1 % Yb, 1% Er: Gd_2O_2S	0.0012±0.0002	0.050±0.007	0.056±0.008	0.10±0.0.02	0.20±0.03
9%Yb, 1% Er:Gd_2O_2S	0.0019±0.0003	0.072±0.009	0.17±0.03	0.15±0.02	0.40±0.06
3%Yb, 7% Er:Gd_2O_2S	0.0014±0.0002	0.079±0.01	0.15±0.02	0.23±0.03	0.46±0.10
2%Yb, 8% Er:Gd_2O_2S	0.0012±0.0002	0.064±0.009	0.12±0.02	0.23±0.03	0.42±0.06
5%Yb, 5% Er:Gd_2O_2S	0.0015±0.0002	0.083±0.01	0.17±0.03	0.22±0.03	0.47±0.10

Table S9 Absolute UC QY for different concentrations of Gd_2O_2S: Yb^{3+} /Er^{3+} at the excitation power density of 3.8 ± 0.57 W/cm^2

QY at 3.8 W/cm²(%)	UV (410 nm)	Green (550 nm)	Red (667 nm)	NIR (822 nm)	Total (QY)%
1 % Yb, 1% Er: Gd_2O_2S	0.0018±0.002	0.069±0.06	0.10±0.02	0.16±0.02	0.82±0.10
2%Yb, 8% Er:Gd_2O_2S	0.002±0.0003	0.10±0.015	0.18±0.10	0.42±0.07	0.70±0.10
3%Yb, 7% Er:Gd_2O_2S	0.010±0.002	0.46±0.07	0.98±0.15	1.23±0.20	2.68±0.40
5%Yb, 5% Er:Gd_2O_2S	0.005±0.0008	0.24±0.04	0.54±0.08	0.44±0.07	1.22±0.20

NOTES and REFERENCES

Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX 78249, USA
Corresponding author: email: pokhrelmadhab@gmail.com

1. K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen and S. R. Lüthi, *Chemistry of Materials*, 2004, **16**, 1244-1251.