

Supplementary Information for

Improved relative temperature sensitivity over 10% K⁻¹ in fluoride nanocrystals via engineering interfacial layer

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Experimental section

Materials. All the raw chemicals, including Calcium carbonate (CaCO_3 , 99.99%, aladdin), Strontium carbonate (SrCO_3 , 99%, Aladdin), Barium carbonate (BaCO_3 , 99.99%, Aladdin), Yttrium oxide (Y_2O_3 , 99.99%, Aladdin), Ytterbium oxide (Yb_2O_3 , 99.99%, Aladdin), Erbium oxide (Er_2O_3 , 99.99%, Aladdin), Neodymium oxide (Nd_2O_3 , 99.99%, Aladdin), Neodymium acetate hydrate ($\text{Nd}(\text{Ac})_3$, 99.9%, Sigma-Aldrich), Ytterbium acetate tetrahydrate ($\text{Yb}(\text{Ac})_3$, 99.99%, Aladdin), oleic acid (OA, 90%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), Oleylamine (OLA, min. 70%, J&K), trifluoroacetic acid (CF_3COOH , TFA, 99.0%, Aladdin) were of analytical grade and were directly used as received without further refinement.

Synthesis of the M-TFA and RE-TFA precursors.

Taking Ca-TFA as an example, 6mmol CaCO_3 and 10 mL distilled water were added in a 50 mL three-neck flask. The mixture was heated to 95°C and then 2.5 mL TFA was added. After all the CaCO_3 powder was completely dissolved and the solution was transparent, the water and remaining TFA were evaporated at 65°C to achieve a powder of 6 mmol Ca-TFA. The procedure for the synthesis of M-TFA and Ln-TFA precursors were similar to the case of Ca-TFA, except the utilization of their corresponding M carbonates or RE oxides with slightly different content.

Synthesis of the RE-OA precursor. Taking Yb-OA as an example, 5 mmol of $\text{Yb}(\text{Ac})_3$ was added in a three-neck flask containing 10 mL OA and 10 mL ODE. The mixture solution was heated to 120 °C under N_2 atmosphere and maintained for 1 h to remove water. After cooling down to room temperature, the slightly viscous precursor liquids were transferred into sample vials for later use. The procedure for the synthesis of Nd-OA precursors were similar to the case of Yb-OA,

Synthesis of core NPs. Taking $\text{SrYbF}_5:40\text{Nd}$ NPs as an example, Sr-TFA (1mmol), Yb-TFA (1mmol \times 0.6), Nd-TFA (1mmol \times 0.4), OA (6 mL), ODE (12 mL) and OLA (2 mL) were added into a 50 mL three-necked flask. The mixture was heated at 120 °C for 90 min to remove water, and then quickly heated to 300 °C under N_2 atmosphere and kept for 120 min. After cooling down to room temperature, the products were precipitated via the addition of ethanol, collected via centrifugation at 12000 rpm for 8

min, washed with cyclohexane and ethanol three times, and finally re-dispersed in 4 mL cyclohexane. The synthetic procedures for other kinds of core NPs were similar to that of SrYbF₅:40Nd NPs.

Synthesis of core/shell NPs. Taking SrYF₅:10Yb2Er@CaF₂ as an example, 2 mmol of Ca-TFA were added into a three-neck flask containing 2 mL OA and 3 mL ODE, and was heated at 120 °C under N₂ for 1 h to remove the remaining water. After cooling down to room temperature, the Ca-TFA precursor solution was transferred into a sample vials for later use. To prepare SrYF₅:10Yb2Er@CaF₂ core/shell NPs, 0.5 mmol (4 mL) SrYF₅:10Yb2Er core NPs, 5 mL OA and 10 mL ODE were added into a 50 mL three-neck flask. After removing cyclohexane at 65 °C for 1 h, the solution was heated to 120 °C under the N₂ and kept for 1.5 h. This solution was heated to 300 °C under N₂ atmosphere, and then the Ca-TFA precursor solution was injected and kept at 300 °C for 1 h.

Synthesis of core/shell/shell NPs. Taking SrYF₅:10Yb2Er@CaF₂@SrYbF₅:40Nd as an example, 6 mmol of Sr-TFA were added into a three-neck flask containing 6 mL OA and 9 mL ODE, and was heated at 120 °C under N₂ for 1 h to remove the remaining water. After cooling down to room temperature, the Sr-TFA precursor solution was transferred into a sample vials for later use. The shell precursor was prepared by mixing the Yb-OA, Nd-OA and the Sr-TFA precursor solutions with a molar ratio of 0.6:0.4:1. To prepare SrYF₅:10Yb2Er@CaF₂@SrYbF₅:40Nd core/shell/shell NPs, 0.5 mmol (4 mL) SrYF₅:10Yb2Er@CaF₂ core/shell NPs, 5 mL OA and 10 mL ODE were added into a 50 mL three-neck flask. After removing cyclohexane at 65 °C for 1 h, the solution was heated to 120 °C under the N₂ and kept for 1.5 h. This solution was heated to 300 °C under N₂ atmosphere, and then 6.5 mL of the shell precursor was injected and kept at 300 °C for 1 h.

Characterizations. X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (Bruker D8 Advance) with a Cu-K α ($\lambda=1.5405$ Å) radiation. The morphology images of the products were characterized by a field emission transmission electron microscopy (FEI Tecnai G2 F20) equipped with an energy dispersive X-ray spectroscopy (EDX, Aztec X-Max 80T). The actual chemical compositions were

determined by an inductively coupled plasma - optical emission spectroscopy (ICP-OES) (Agilent 720ES, Plasma flow: 15.0L/min, Sample uptake delay: 15s, Replicate read time: 2s). UC emission spectra were carried out on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with an adjustable laser diode (980 nm) and temperature controlling stage. Raman spectra were recorded by a micro-Raman spectrometer (Renishaw, inVia-Reflex) at room temperature in the frequency range of 150–1000 cm^{-1} under the excitation of 532 nm laser.

Table S1. Comparison of temperature sensitivities of different reported ratiometric thermometers.

Materials	Temperature range (K)	S_a -max(K ⁻¹)	S_r -max(%K ⁻¹)	Ref.
Sr ₄ La(PO ₄) ₃ O:Eu ²⁺ /Sm ³⁺	293-573	/	0.48	S1
Ca ₈ ZnLa(PO ₄) ₇ :Tb ³⁺ ,Eu ³⁺	298-448	0.34	0.53	S2
Y ₃ Al ₅ O ₁₂ :Ti ³⁺ ,Ti ⁴⁺	123-573	/	0.71	S3
YNbO ₄ :Pr ³⁺ ,Tb ³⁺	293-508	0.0125	1.01	S4
Ca ₁₄ Al ₁₀ Zn ₆ O ₃₅ :Bi ³⁺ ,Mn ⁴⁺	303-563	0.015	1.21	S5
LuNbO ₄ :Pr ³⁺ ,Tb ³⁺	283-493	0.024	1.26	S6
Zn ₂ GeO ₄ :Mn ²⁺ ,Eu ³⁺	293-353	/	1.96	S7
LaPO ₄ :Yb ³⁺ ,Tm ³⁺ ,Eu ³⁺	293-679	/	2.4	S8
Ca ₂ Al ₂ SiO ₇ :Eu ²⁺ ,Eu ³⁺	303-443	0.024	2.46	S9
La _{1-y} Gd _y AlO ₃ :Eu ²⁺ ,Eu ³⁺	303-473	0.084	3.233	S10
Zn ₂ SiO ₄ :Mn ²⁺ /Gd ₂ O ₃ :Eu ³⁺	303-623	0.073	3.05	S11
CaNb ₂ O ₆ :Bi ³⁺ ,Eu ³⁺	298-523	0.122	3.793	S12
GdNbO ₄ :Bi ³⁺ ,Eu ³⁺	303-523	0.037	3.81	S13
ZrO ₂ :Ti ⁴⁺ ,Eu ³⁺	3.3-413	0.414	3.84	S14
Li ₂ TiO ₃ :Mn ⁴⁺ and Y ₂ O ₃ :Dy ³⁺	273-373	0.0263	4.43	S15
Y ₂ O ₃ :Ho ³⁺ and Mg ₂ TiO ₄ :Mn ⁴⁺	303-373	/	4.60	S16
Y ₃ Al ₅ O ₁₂ :Eu ³⁺ ,Mn ⁴⁺	293-393	0.444	4.81	S17
LiTaO ₃ :Ti ⁴⁺ ,Eu ³⁺	303-443	0.397	5.425	S18
Ca ₂ MgWO ₆ :Bi ³⁺ ,Eu ³⁺	298-523	0.961	8.52	S19
NaYF ₄ :60%Yb ³⁺ ,4%Nd ³⁺ @ NaYF ₄ @NaYF ₄ :20%Yb ³⁺ , 2%Er ³⁺	293-413	/	9.60	S20
SrYF ₅ :10Yb2Er@CaF ₂ @ SrYbF ₅ :40Nd	303-413	2.56	10.01	This work

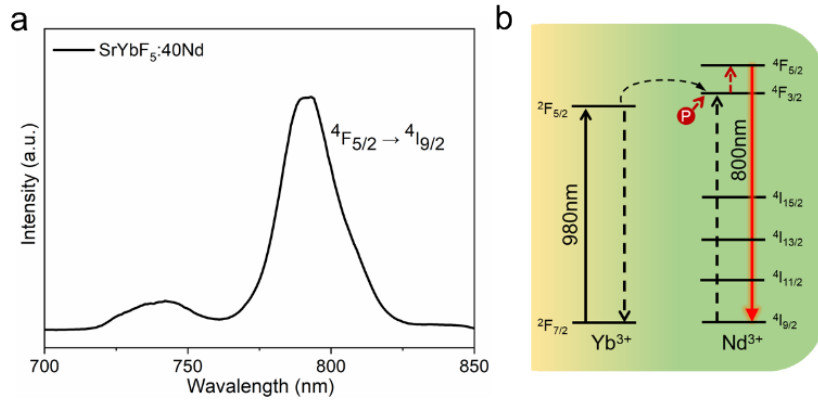


Figure S1. (a) UC emission spectra of the SrYbF₅:40Nd NCs excited by 980 nm NIR light. (b) Proposed energy transfer UC mechanism between the Yb³⁺ and Nd³⁺ codopants.

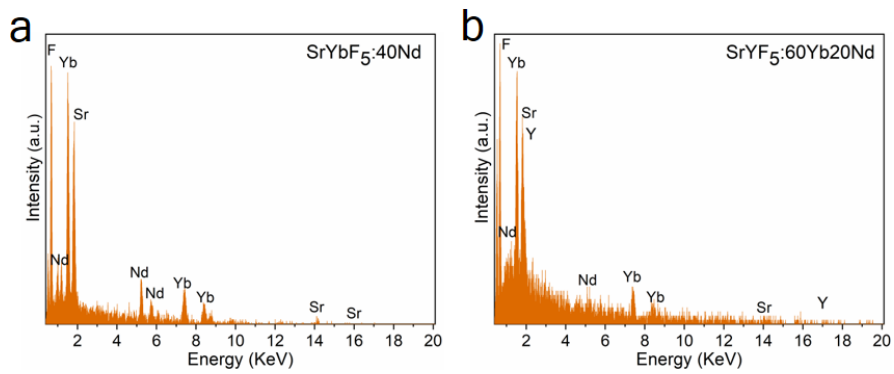


Figure S2. EDX spectra of (a) SrYbF₅:40Nd and (b) SrYF₅:60Yb20Nd NCs.

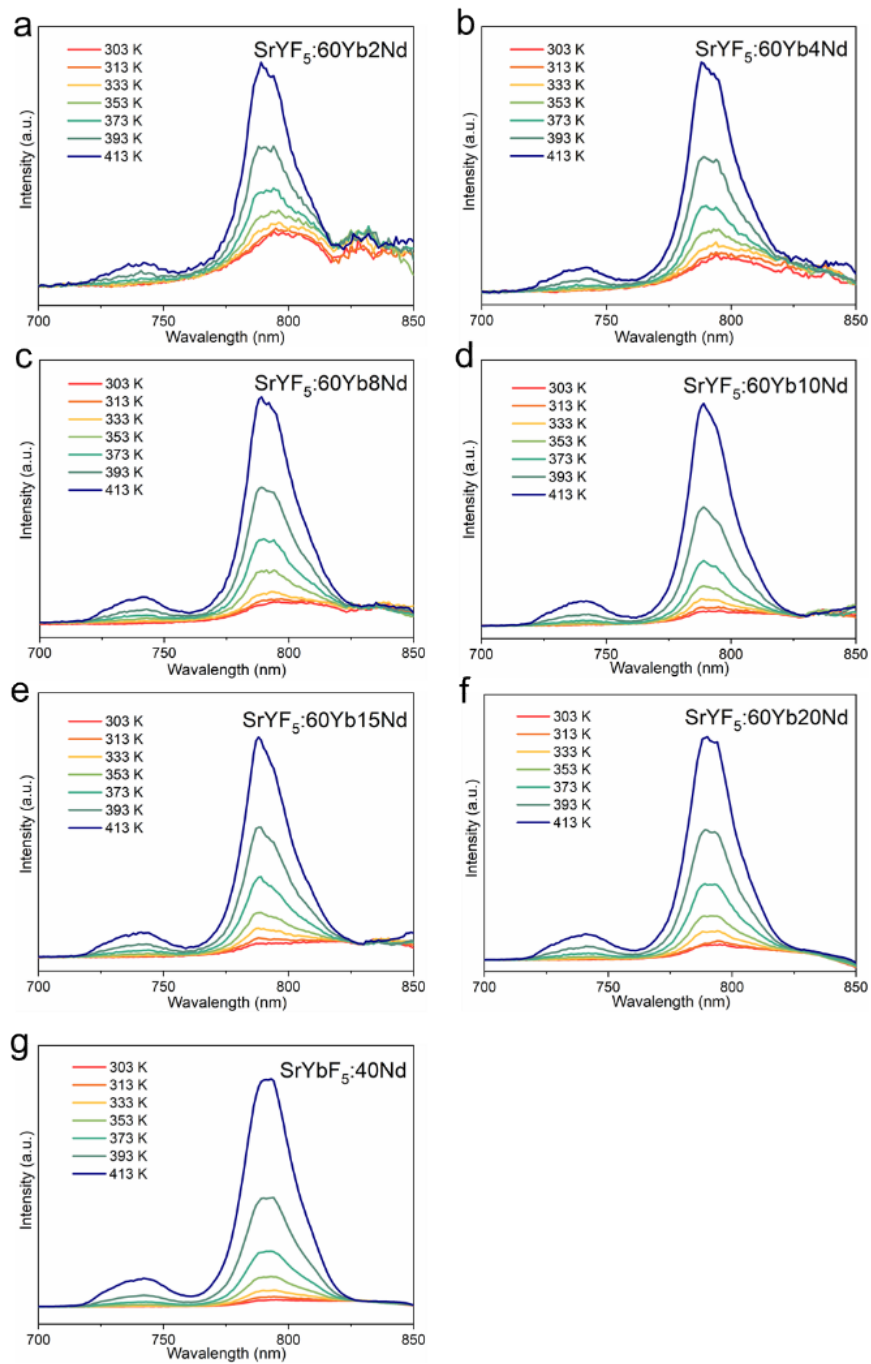


Figure S3. UC emission spectra of the SrYF₅:60Yb/Nd with increasing the Nd³⁺ ions concentration from 2 to 40 mol%.

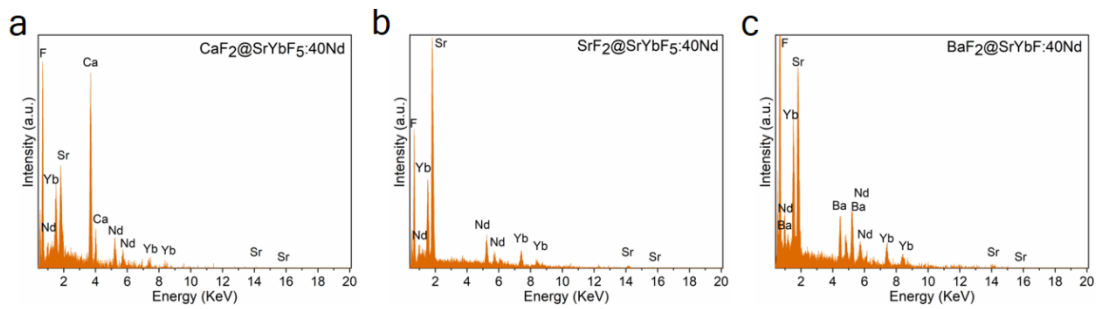


Figure S4. EDX spectra of the $\text{CaF}_2@SrYbF_5:40Nd$, $\text{SrF}_2@SrYbF_5:40Nd$ and $\text{BaF}_2@SrYbF_5:40Nd$ NCs.

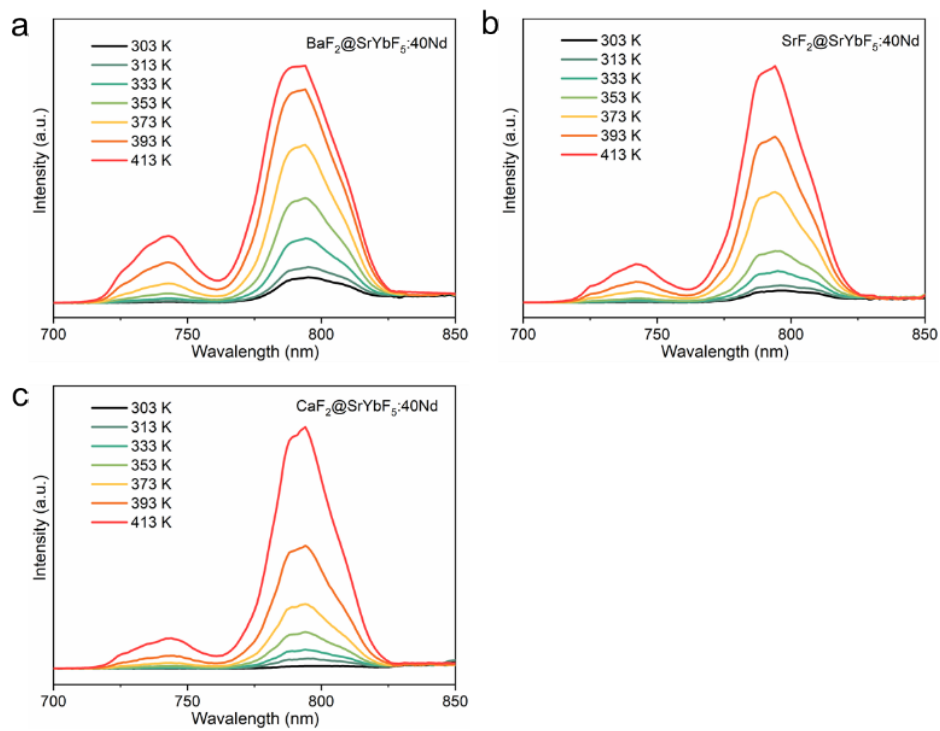


Figure S5. Temperature dependent UC emission spectra of (a) $\text{BaF}_2@SrYbF_5:40Nd$, (b) $\text{SrF}_2@SrYbF_5:40Nd$ and (c) $\text{CaF}_2@SrYbF_5:40Nd$ NCs.

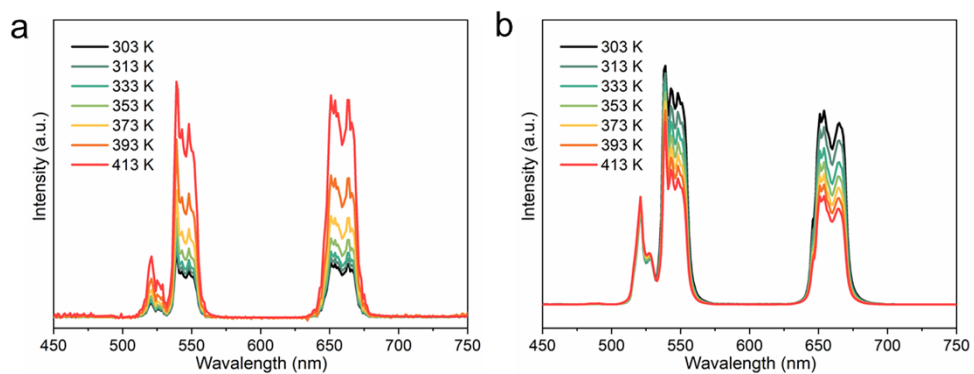


Figure S6. Temperature dependent UC emission spectra of (a) $\text{SrYbF}_5:20Yb2Er$ and (b) $\text{SrYbF}_5:20Yb2Er@CaF_2$.

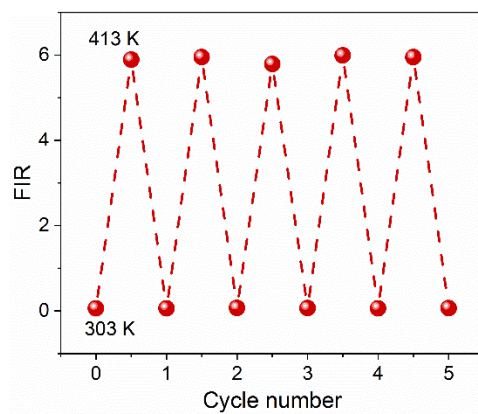


Figure S7. LIR of the SrYF₅:10Yb₂Er@CaF₂@SrYbF₅:40Nd at 303 K and 413 K within five cycles.

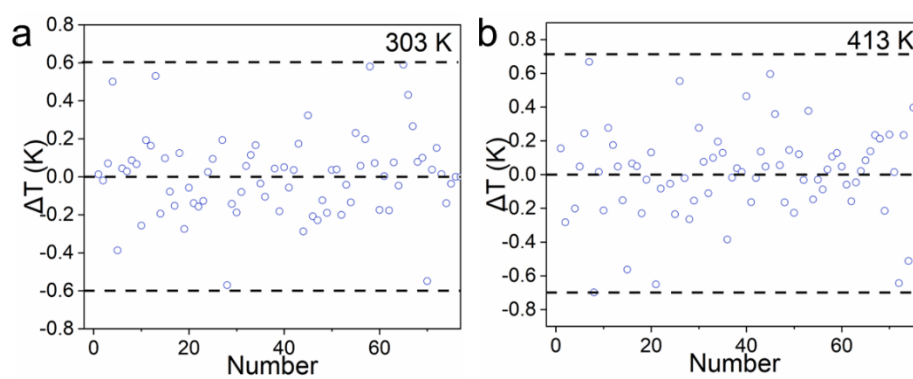


Figure S8. Calculated ΔT at 303 (a), and 413 K (b) based on the experimental results of each cycle.

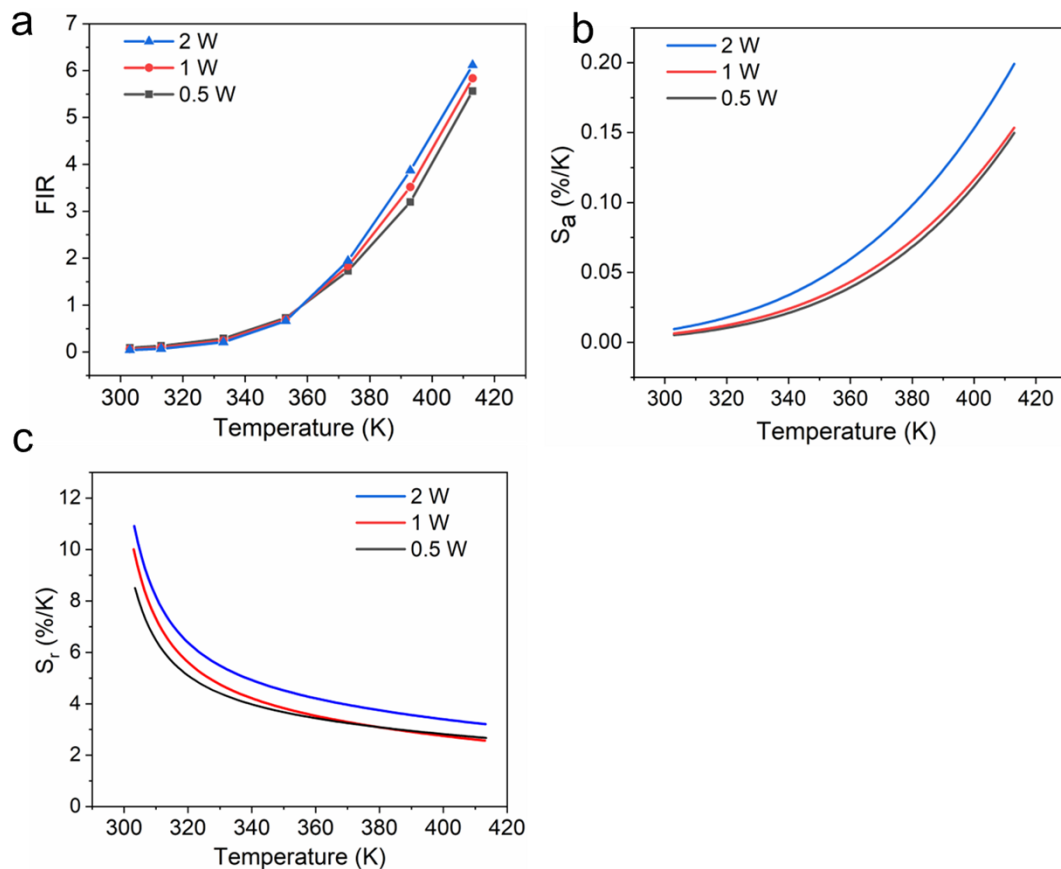


Figure S9 (a) Pumping power dependence FIR, calculated S_a (b) and S_r (c) of the $\text{SrYF}_5:10\text{Yb}_2\text{Er}@\text{CaF}_2@\text{SrYbF}_5:40\text{Nd}$.

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