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Supplementary Materials

Temperature sensitive cross relaxation between Er^{3+} ions in laminated hosts: a novel mechanism for thermochromic upconversion and high performance thermometry

Feng Huang[a,b,c,] *, *Ting Yang*[a,b,c], *Shaoxiong Wang*[a,b,c], *Lin Lin*[a,b,c], *Tao Hu*[d],

Daqin Chen[a,b,c,] *

[a] College of Physics and Energy, Fujian Normal University, Fujian Provincial Key Laboratory of Quantum Manipulation and New Energy Materials, Fuzhou, 350117, China
[b] Fujian Provincial Engineering Technology Research Center of Solar Energy Conversion and Energy Storage, Fuzhou,350117, China.
[c] Fujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, 361005, China
[d] Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, University of Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China
Email: fengh@fjnu.edu.cn, dqchen@fjnu.edu.cn.

Figure S1-S9

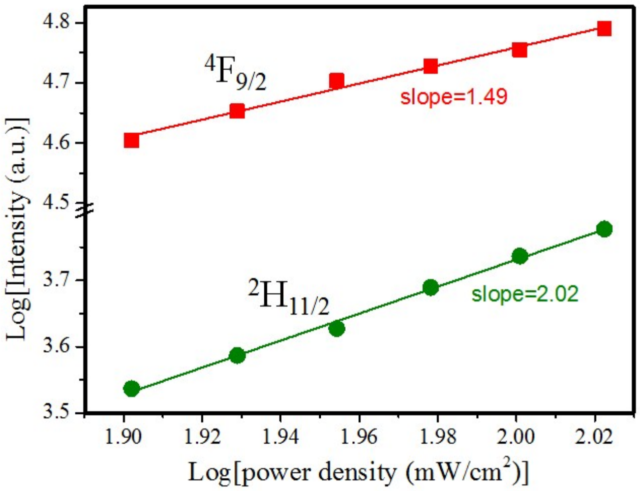

Figure S1. Logarithmic dependence of $^2H_{11/2}$ (green) and $^4F_{9/2}$ (red) emission intensities on power density of excitation

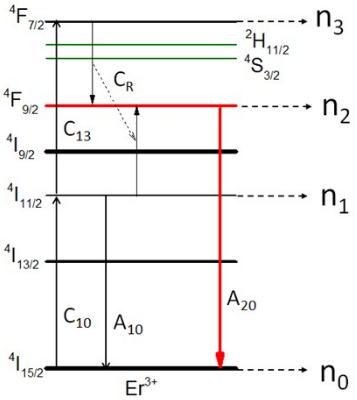

Figure S2. A simplified model for establishing the rate equations and calculating the power dependence of the $^4F_{9/2}$ emission, in the presence of $^4F_{7/2}+^4I_{11/2}\rightarrow^4F_{9/2}+^4F_{9/2}$ cross relaxation.

According to the simplified model displayed in Figure S2, The rate equation is established as following:

$$\frac{dn_1}{dt}=C_{10}Pn_0-A_{10}n_1-C_{13}Pn_1-C_Rn_1n_3$$

$$\frac{dn_2}{dt}=2C_Rn_1n_3-A_{20}n_2$$

$$\frac{dn_3}{dt}=C_{13}Pn_1-C_Rn_1n_3$$

Where n_0, n_1, n_2 and n_3 is the population at the $^4I_{15/2}$, $^4I_{11/2}$, $^4F_{9/2}$ and $^4F_{7/2}$, A_{10} and A_{20} is the radiative transition probability of $^4I_{11/2}$ and $^4F_{9/2}$, C_{10} and C_{13} is the cross section of the $^4I_{11/2}$ and $^4F_{9/2}$ for absorbing a 980 nm photon, while C_R is the probability for the $^4F_{7/2}+^4I_{11/2}\rightarrow^4F_{9/2}+^4F_{9/2}$ cross relaxation, and P is the pump power.

After solving the above simultaneous differential equations, the population of $^4F_{9/2}$ (n_2) can be expressed as following:

$$n_2=\frac{2C_{10}C_{13}n_0P^2}{A_{20}(A_{10}+2C_{13}P)}$$

Compared with regular upconversion materials, in which the population always possess a two order power dependence ($n\propto P^2$), in this case the population of $^4F_{9/2}$ shows a relatively lower order dependence on the pump power.

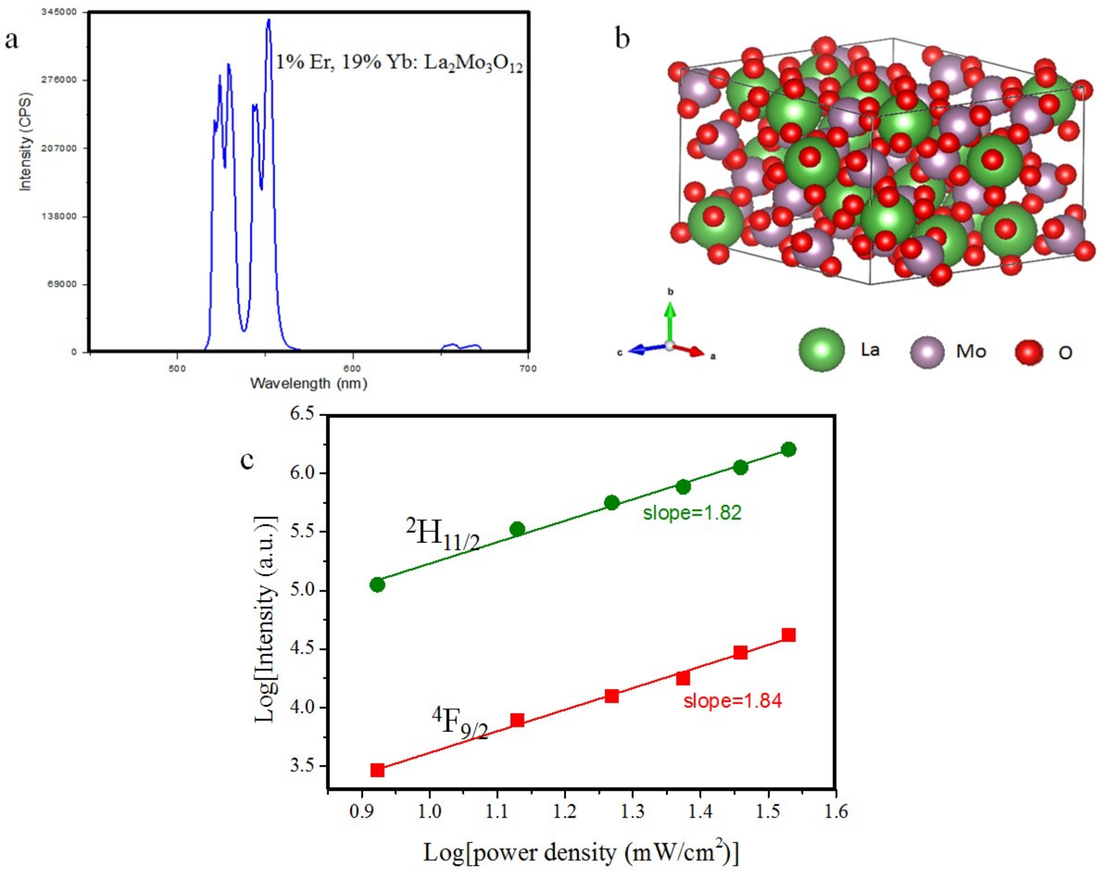

Figure S3. (a) 980 nm laser excited upconversion spectra of the $La_2(MoO_4)_3$ phosphors doped with 1% Er^{3+} and 19% Yb^{3+}, (b) schematic displaying the lattice structure of the $La_2(MoO_4)_3$ phosphor, (c) Logarithmic dependence of $^2H_{11/2}$ (green) and $^4F_{9/2}$ (red) emission intensities on power density.

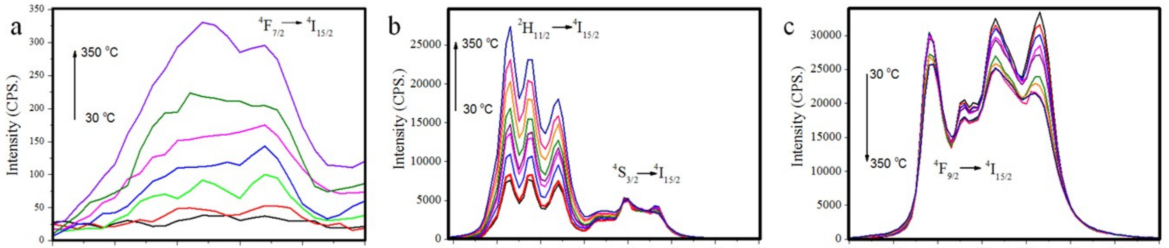

Figure S4. Enlarged upconversion spectra showing the detailed temperature dependence of the emission ascribing to (a) $^4F_{7/2}$, (b) $^2H_{11/2}$ and $^4S_{3/2}$, as well as (c) $^4F_{9/2}$ to ground state of Er^{3+}, respectively.

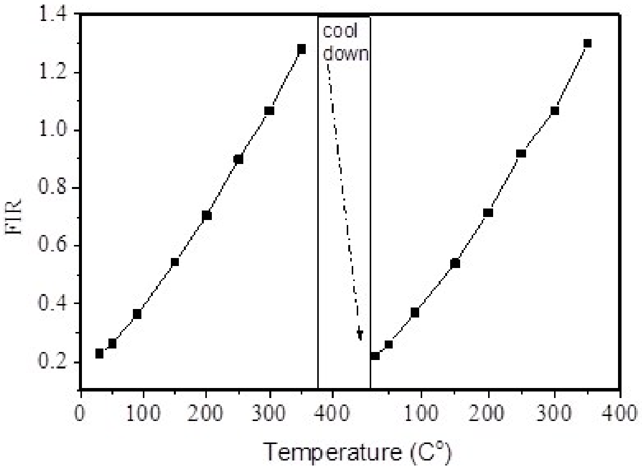

Figure S5. FIR variation with the temprature in two rounds of emperature-recycle measurements

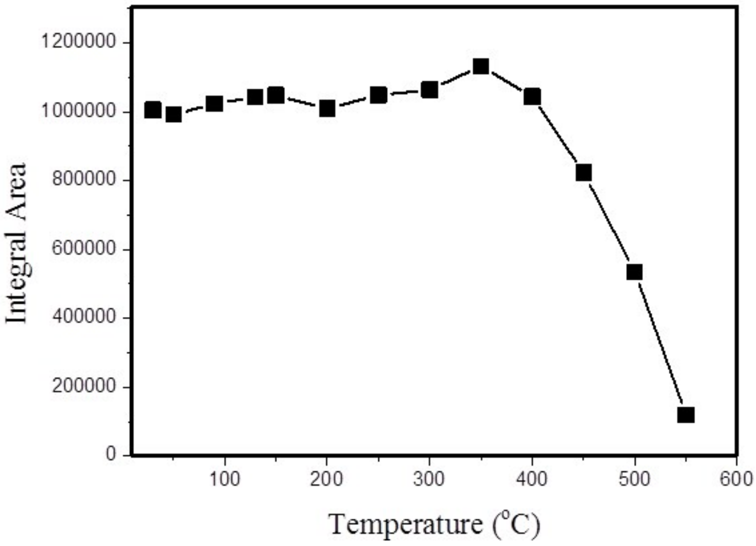

Figure S6. Integral area of the temperature dependent upconversion spectra of the 19% Yb, 1% Er doped La_2MoO_6 sample

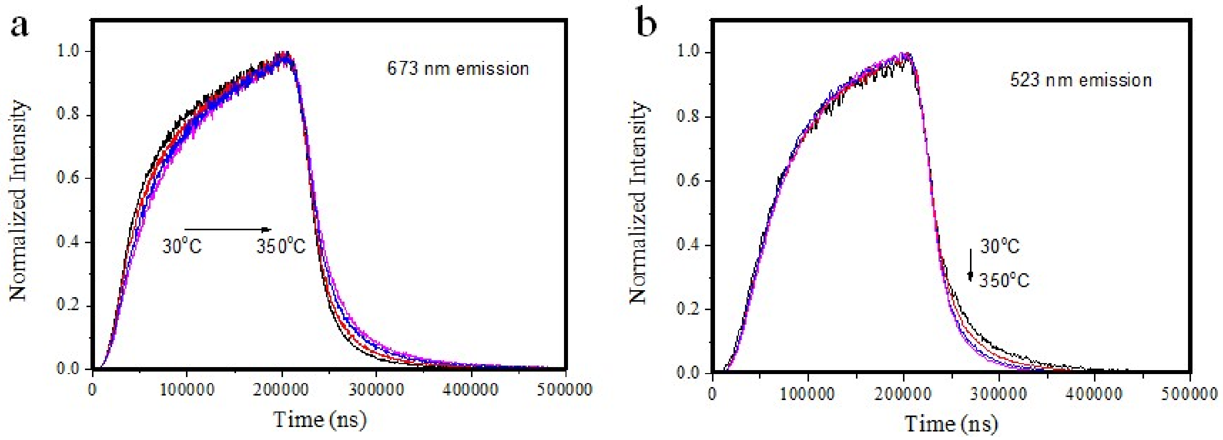

Figure S7. Normalized time-resolved upconversion luminescent intensity for the (a) $^2H_{11/2}$ and (b) $^4F_{9/2}$ levels monitored at various temperature (30 ℃ to 350 ℃), excited by a pulse 980 nm laser, with the pulse width of 200 μs.

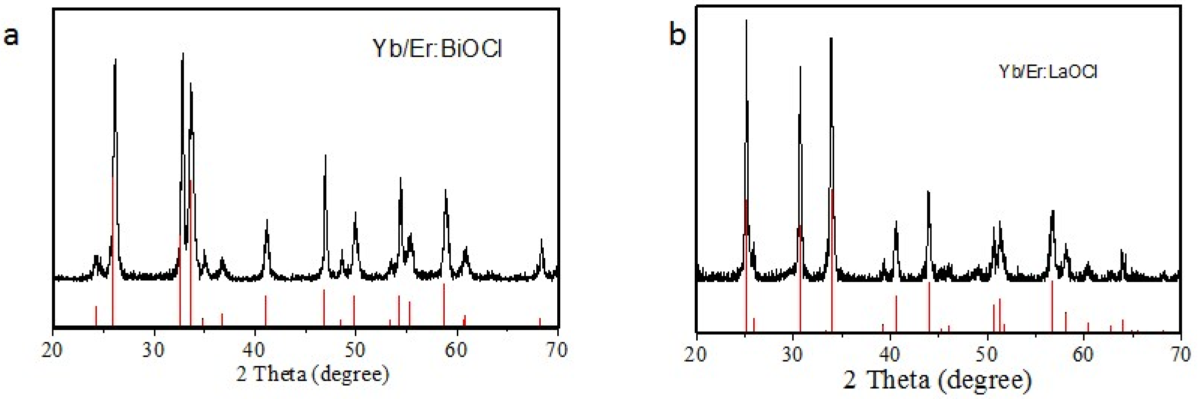

Figure S8. XRD patterns of the prepared (a) Yb/Er:BiOCl and (b) Yb/Er:LaOCl samples; bars on the bottoms and the standard data for BiOCl (PDF 73-2060) and LaOCl (PDF 88-0064)

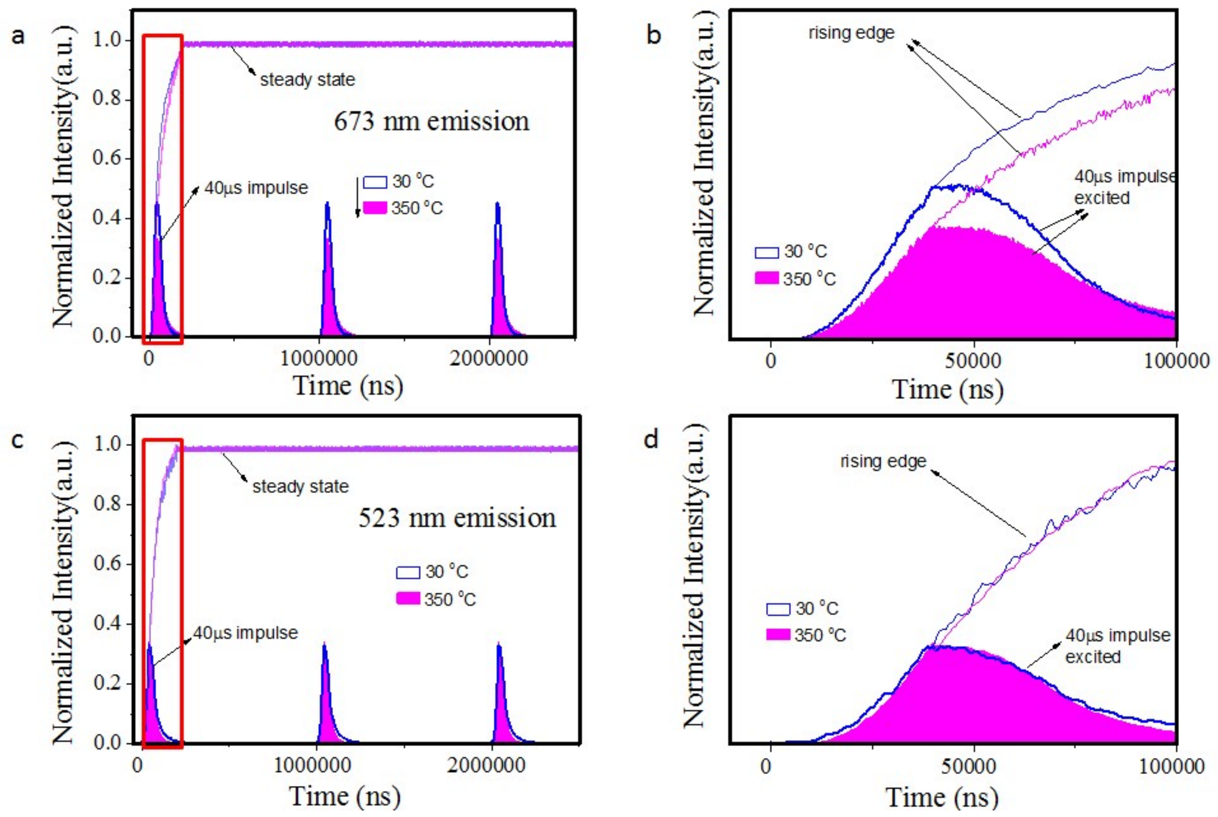

Figure S9. Curves of luminescent intensity versus time for the (a) 673 nm and (c) 523 nm emissions, excited by steady state laser and impulse laser with pulse with of 40 µs and period of 1 ms, (b) and (d) enlarge patterns corresponding to the red framed regions in (a) and (b), respectively.

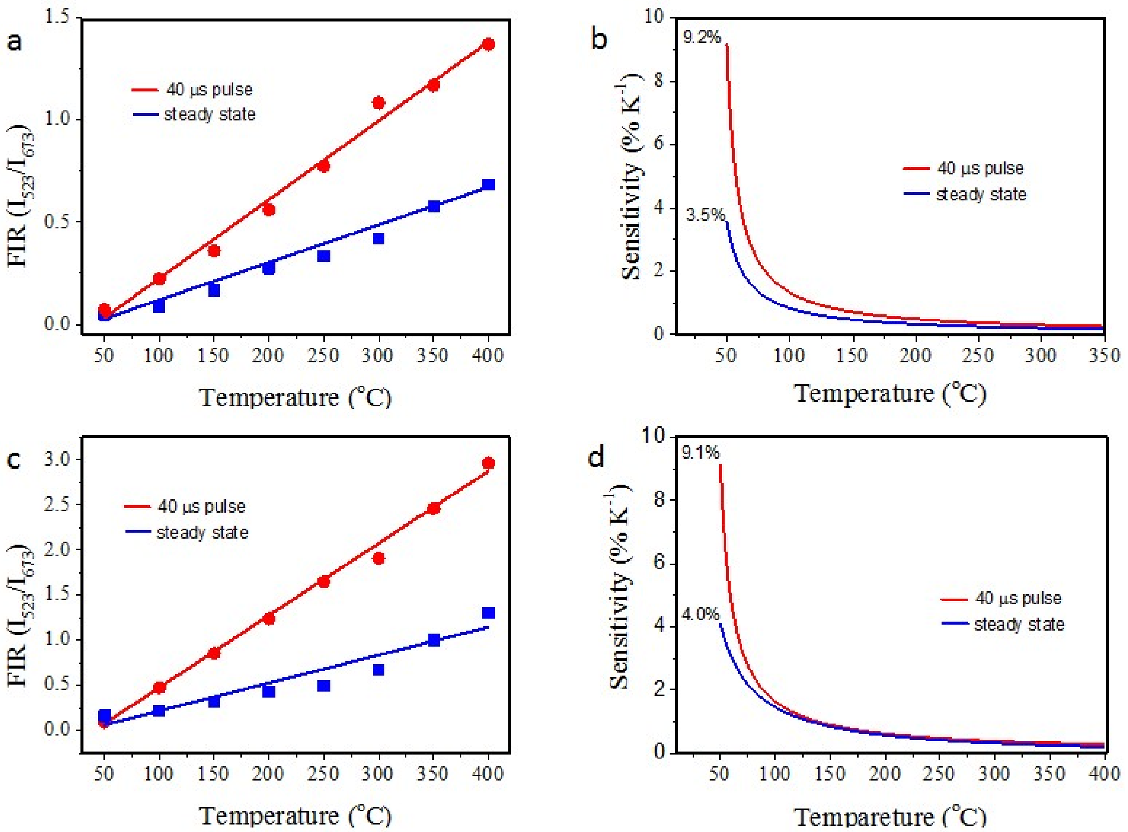

Figure S10. Plots of FIR versus temperature for the (a) Yb/Er:LaOCl and (c) Yb/Er:BiOCl samples excited by steady state and impulse laser with pulse widths of 40 µs, lines are the corresponding linear fitting data; (b) and (d) are the calculated relative temperature sensitivity corresponding to the data presented in (a) and (b).

Table S1. The optical thermometric parameters of Yb/Er:La_2MoO_6, Yb/Er:LaOCl and Yb/Er:BiOCl

Phosphors	Steady State Pumped		Impulse Pumped (plus width of 40 µs)	
	Slopes of FIR vs T (10^{-3} K^{-1})	Maximum S_r (K^{-1})	Slopes of FIR vs T (10^{-3} K^{-1})	Maximum S_r (K^{-1})
Yb/Er:La_2MoO_6	3.3	1.6%	4.5	3.3%
Yb/Er:LaOCl	1.8	3.5%	3.8	9.2%
Yb/Er:BiOCl	3.0	4.0%	8.0	9.1%

Supplementary Note 1: Theoretical evaluation for the relationship between the probability of $^4F_{7/2}$+$^4I_{11/2}$→$^4F_{9/2}$+$^4F_{9/2}$ cross relaxation and the temperature change

Herein, the $^4F_{7/2}$+$^4I_{11/2}$→$^4F_{9/2}$+$^4F_{9/2}$ cross relaxation is a typical fluorescence resonance energy transfer (FRET) through dipole-dipole interaction. The probability of this cross relaxation is noted as C_r. According to the principle of dipole-dipole interaction, its value is related to the average distance between Er ions (R) as,

$$C_r \propto \frac{1}{R^6}$$

In the other hand, the value of R is variable with the temperature change (Δ T),

$$R = R_0(1 + \alpha\Delta T)$$

where α is the linear thermal expansion coefficients of the host, R_0 is the average distance at room temperature. Therefore, the probability of this cross relaxation can be written as

$$C_r \propto \frac{1}{{R_0}^6(1 + \alpha\Delta T)^6}$$

Obviously, this is not a linear relationship. But owing to the reason that the term $\alpha\Delta T$ is much smaller than 1, herein we can conduct Taylor expansion to this expression as follow:

$$C_r \propto \frac{1}{{R_0}^6}[1 - 6\alpha\Delta T + 21(\alpha\Delta T)^2......]$$

By ignoring the high order term, the relationship between cross relaxation and temperature can be approximatively considered as a linear relationship.

$$C_r \propto \frac{1}{{R_0}^6}(1 - 6\alpha\Delta T)$$