Supporting Information

Investigation on the fluorescence intensity ratio sensing thermometry based on non-thermally coupled levels

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1. EXPERIMENTAL SECTION

Synthesis of $YbPO_4$:Ln^{3+} (Ln^{3+}=Tm^{3}+, Er^{3+}, Ho^{3+}, Tm^{3+}/Er^{3+}, Tm^{3+}/Ho^{3+})

The $YbPO_4$ was synthesized by the method of co-precipitation. The rare earth nitrate solutions were mixed according to the chemical formulas with stirring. After that, the mixed solution of nitrate was dropped into the water solution of diammonium phosphate slowly and stirred at 25 °C for 7 h. Then, the produces were separated through centrifugation and carefully washed two times with deionized water and ethyl alcohol respectively. Finally, the precipitates were dried at 60 °C for 12 h, and then calcined at 1200 °C for 2 h.

Synthesis of $NaYb(MoO_4)_2$:Ln^{3+} (Ln^{3+}=Tm^{3+}, Er^{3+}, Ho^{3+}, Tm^{3+}/Er^{3+}, Tm^{3+}/Ho^{3+})

They were synthesized by hydrothermal method. Taking $NaYb(MoO_4)_2$ as an example: First, we mixed nitrate solutions. Then Na_2MoO_4 aqueous solution was added drop wise into the $Ln(NO_3)_3$ solutions and adjusted the pH value to 5 to form a white colloidal solution. After magnetic stirred for 1 h, the above solution was transferred to a Teflon bottle in a stainless steel autoclave, sealed and temperature kept in 180 °C for 24 h. After the autoclave was cooled to room temperature, the produces were separated through centrifugation and carefully washed two times with deionized water and ethyl alcohol, respectively. Finally, the precipitates were dried at 60 °C for 10 h, and then calcined at 600 °C for 6 h, finally naturally cooled to room temperature.

Synthesis of Y_2O_3:Yb_{3+},Ln_{3+} and $LaAlO_3$:Yb_{3+}, Ln_{3+} (Ln^{3+}=Tm^{3}+, Er^{3}+, Ho^{3+}, Tm^{3+}/Er^{3+}, Tm^{3+}/Ho^{3}+)

They were synthesized by sol-gel. Taking Y_2O_3 as an example: The rare earth nitrate solutions were mixed according to the chemical formulas with stirring. Next, the chelating agent $C_6H_8O_7 \cdot H_2O$ was added to above solution with molar ratio 2:1 of citric acid to total metal ions. The mixture was stirred until formed a highly transparent solution. Then, dried at 120 °C for 12 h, heated at 500 °C for 2 h. Finally, heated in air at 1200 °C for 4 h, after that ground in an agate mortar.

The synthesis of $LaAlO_3$ followed the similar procedure. The difference for $LaAlO_3$ is heated in air at 900 °C for 4 h. Detailed information can be found in Reference.

Synthesis of $BaTiO_3$:Yb^{3+}, Ln^{3+} (Ln^{3+}=Tm^{3+}, Er^{3+}, Ho^{3+}, Tm^{3+}/Er^{3+}, Tm^{3+}/Ho^{3+})

The $BaTiO_3$ was synthesized by the method of sol-gel. Suitable proportion of $Ba(CH_3COO)_2$ and $Ln(NO)_3$ were dissolved in deionized water (7.20 mL) in a beaker marked A, and the mixture was stirred to form a transparent solution. $Ti(OC_4H_9)_4$ (10 mmol), CH_3COOH (5.14 mL) and ethanol (3.33 mL) were mixed in another beaker marked B. A solution was dropped into B solution and stirred for 40 min at 50 °C. After being aged for 2 h at 50 °C, it turned into gels. The gels were dried for 10 min at 150 °C and then calcined at 900 °C for 2 h, after that ground in an agate mortar.

2. FIGURES

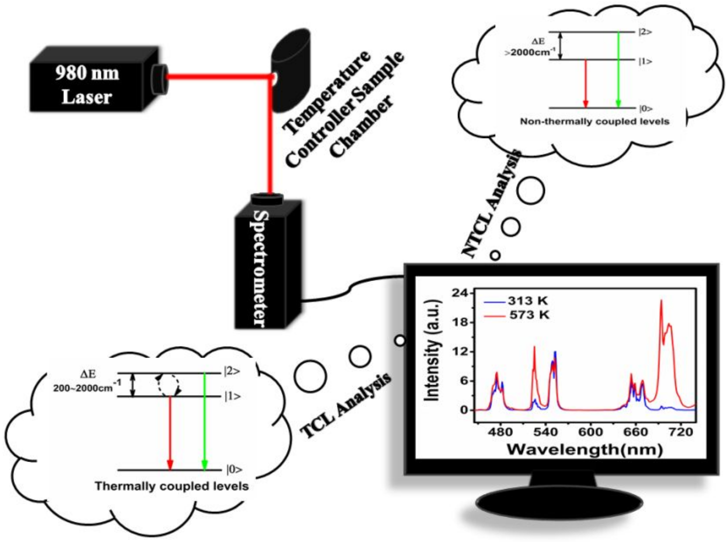

Figure S1. Schematic illustration of the fluorescence intensity ratio sensing thermometry based on non-thermally coupled levels.

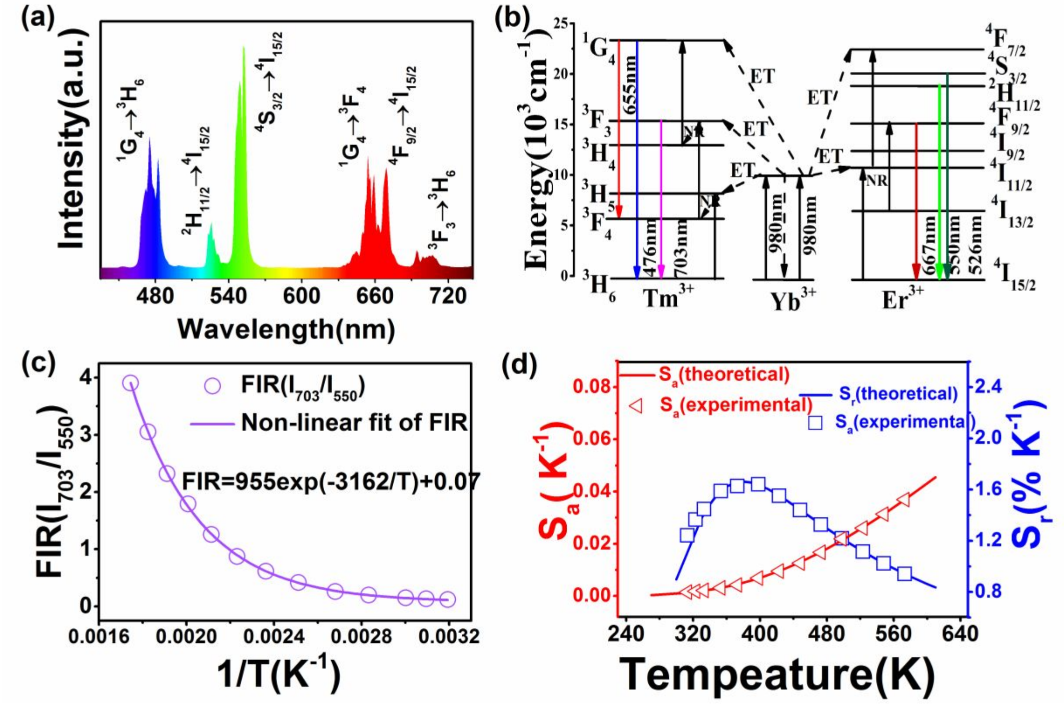

Figure S2. (a) The upconversion luminescence (UCL) spectrum of $YbPO_4$:Tm^{3+}/Er^{3+} under excitation of 980 nm; (b) The energy level diagram; (c) Experimental measured and theoretical fitted FIR (I_{703}/I_{550}) plots of NTCLs based on $YbPO_4$: Tm^{3+}/Er^{3+} versus temperature; (d) The corresponding S_a and S_r versus temperature.

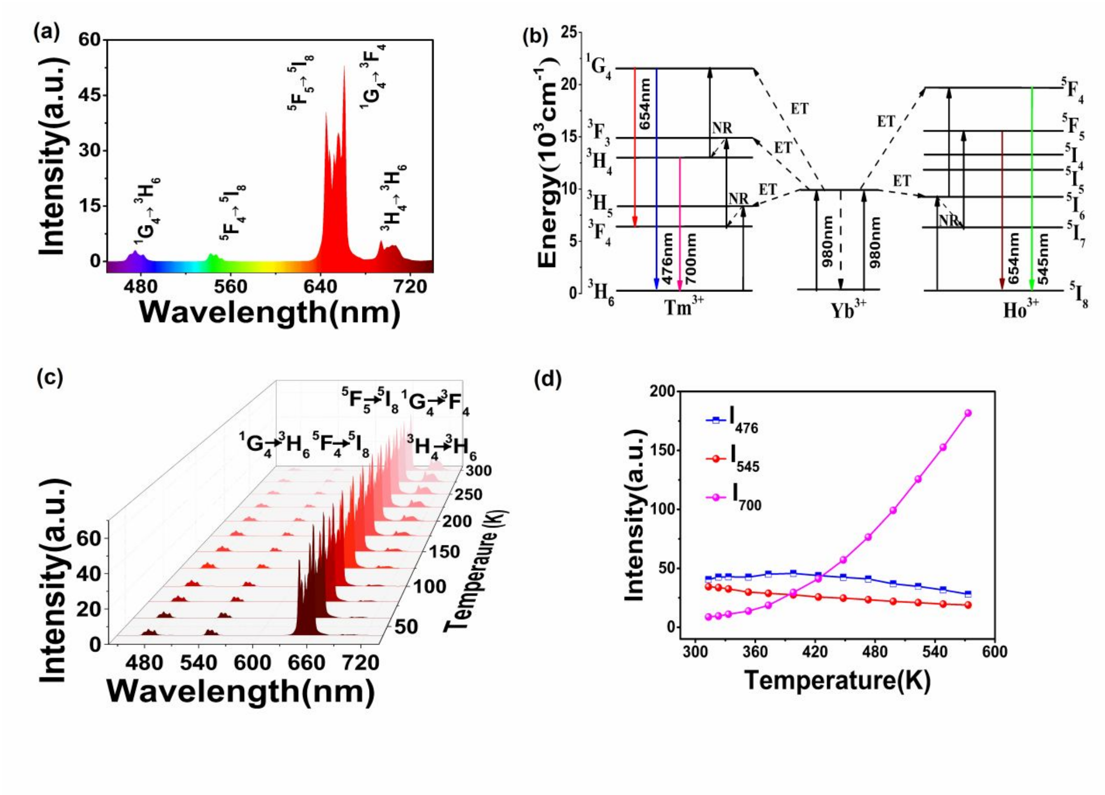

Figure S3. (a) The upconversion luminescence (UCL) spectrum of $YbPO_4$: Tm^{3+}/Ho^{3+} under excitation of 980 nm; (b) The energy level diagram; (c) Temperature-dependent UCL spectra recorded from 313 to 573 K; (d) Polyline displaying the luminescence intensity of 476 nm, 545 nm and 700 nm at various temperatures.

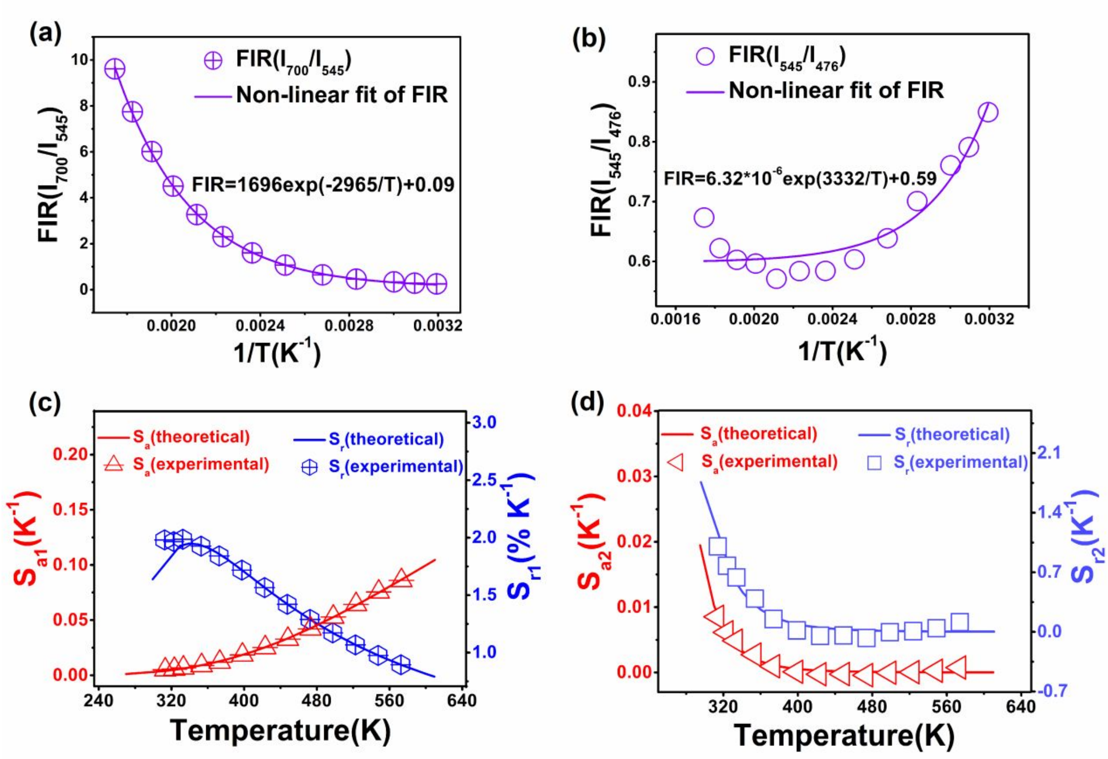

Figure S4. Experimental measured and theoretical fitted (a) FIR (I_{700}/I_{545}), (b) FIR (I_{545}/I_{476}) plots of NTCLs based on $YbPO_4$: Tm^{3+}/Ho^{3+} versus temperature, and the corresponding (c) S_a and (d) S_r versus temperature.

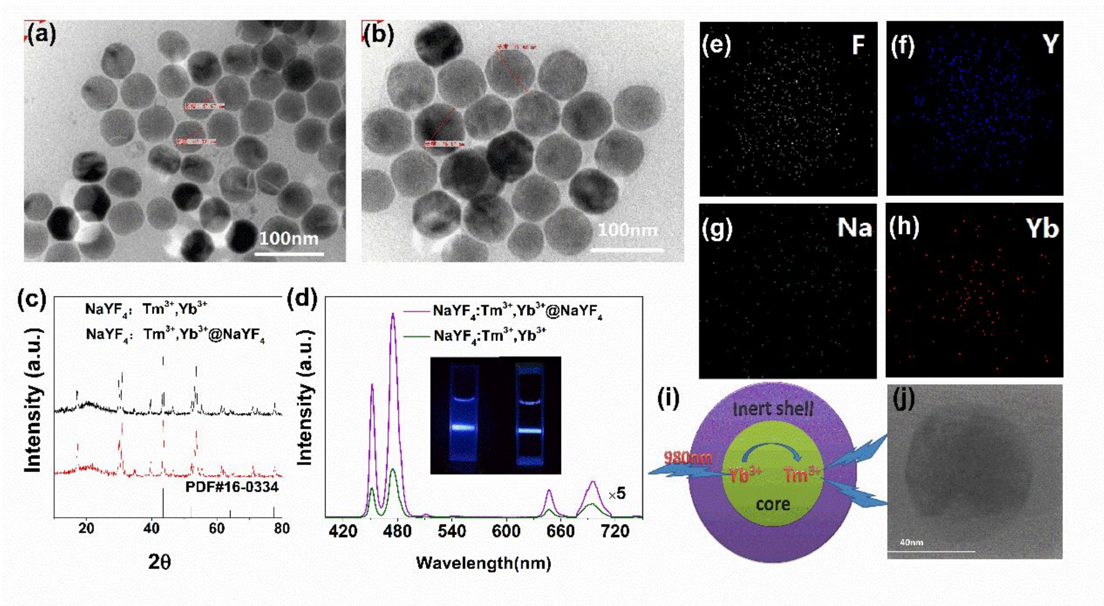

Figure S5. (a) TEM image of $NaYF_4$ core; (b) TEM image of $NaYF_4$:Tm^{3+},Yb^{3+}@$NaYF_4$ core-shell; (c) XRD pattern and standard diffraction pattern; (d) Luminescence spectra of $NaYF_4$:Tm^{3+},Yb^{3+} core and $NaYF_4$:Tm^{3+},Yb^{3+}@$NaYF_4$ core-shell nanoparticles dispersed in cyclohexane solutions, Insets: two typical photographs showing the luminescence of the core-shell (left) and core (right) nanocrystals; (e–h,j) Mapping images $NaYF_4$:Tm^{3+},Yb^{3+}@$NaYF_4$; (i) Schematic illustration of the $NaYF_4$:Tm^{3+},Yb^{3+}@ $NaYF_4$ core-shell structure.

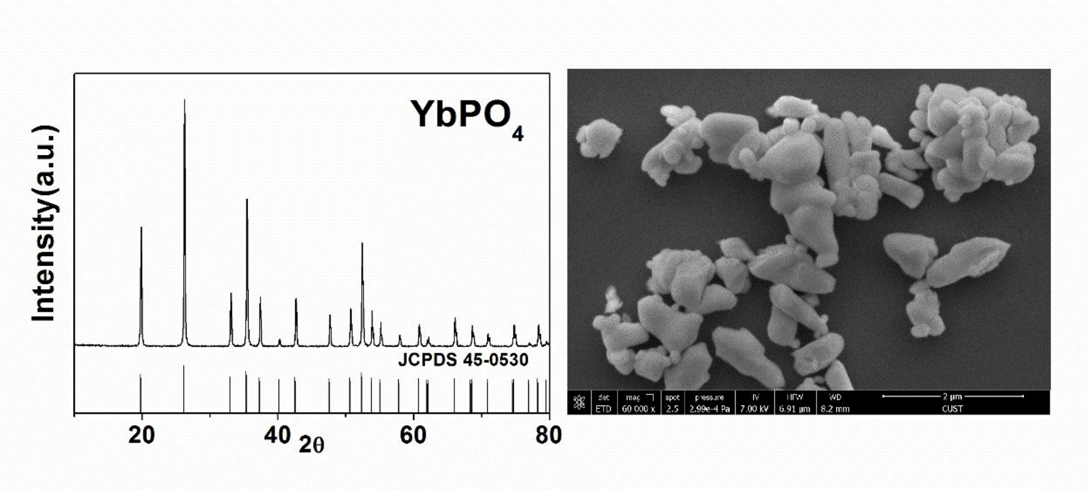

Figure S6. The XRD (left) and SEM image (right) of $YbPO_4$.

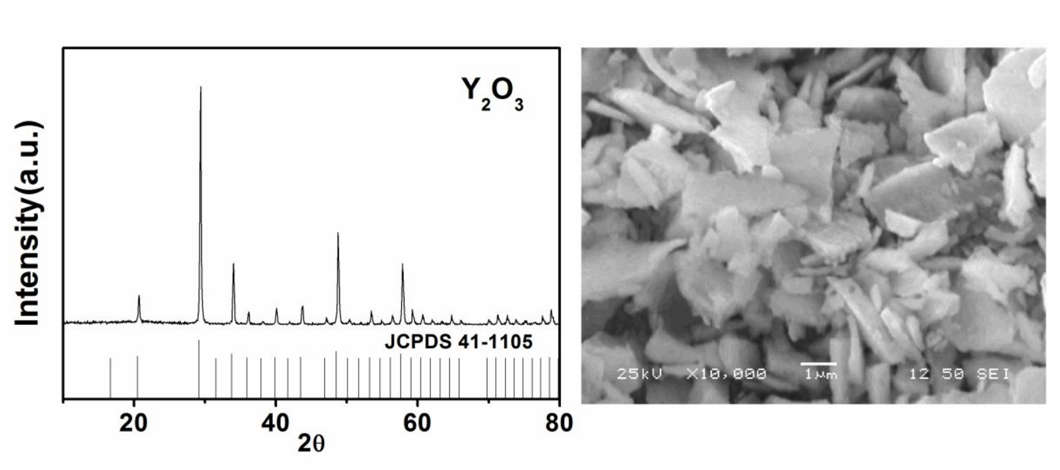

Figure S7. The XRD (left) and SEM image (right) of Y_2O_3.

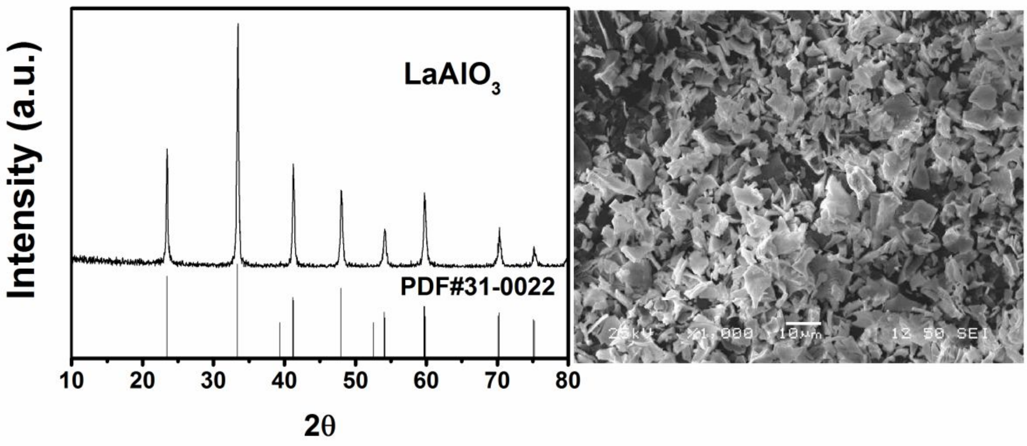

Figure S8. The XRD (left) and SEM image (right) of Y_2O_3.

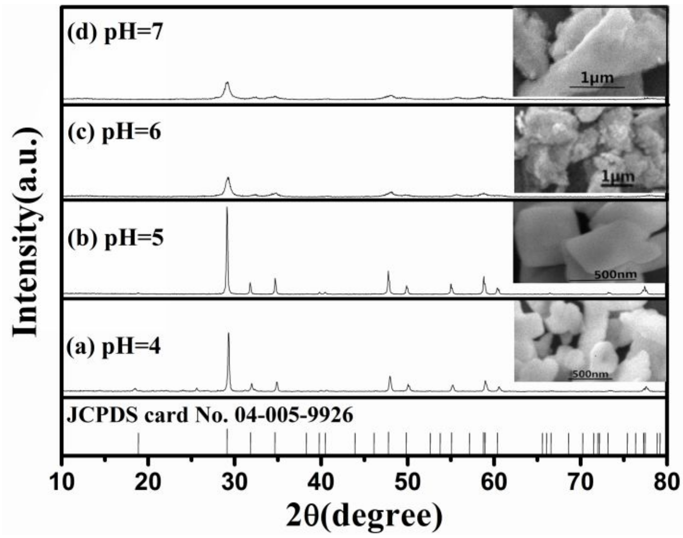

Figure S9. The XRD of $NaYb(MoO_4)_2$ samples prepared at the value of pH from 4 to 7. Insets show the SEM images of the corresponding samples.

3. TABLES

Table S1. The temperature sensitivity (S_a, S_r) comparison by using NTCL-FIR temperature sensing method and TCL-FIR method.

Max.S [%K^{-1}]		$YbPO_4$: Tm^{3+}	$NaYb(MoO_4)_2$:Tm^{3+}	$BaTiO_3$: Tm^{3+},Yb^{3+}	$LaAlO_3$: Tm^{3+},Yb^{3+}	Y_2O_3: Tm^{3+},Yb^{3+}
S_a	NTCL	44.90	38.80	25.12	4.10	6.66
	TCL	0.55	0.25	0.41	0.21	0.24
S_r	NTCL	1.85	2.83	2.12	1.38	1.05
	TCL	0.27	0.36	0.33	0.29	0.65

Table S2. The minimum temperature accuracy (δT) comparison by using NTCL-FIR temperature sensing method and TCL-FIR method.

Min.δT [K]		$YbPO_4$:Tm^{3+}	$NaYb(MoO_4)_2$:Tm^{3+}	$BaTiO_3$:Tm^{3+},Yb^{3+}	$LaAlO_3$:Tm^{3+},Yb^{3+}	Y_2O_3:Tm^{3+},Yb^{3+}
δT	**NTCL**	**0.27**	**0.18**	**0.24**	**0.36**	**0.47**
	TCL	**1.85**	**1.39**	**1.53**	**1.71**	**0.77**

Table S3. Summary of some significant thermometry parameters (S_a, S_r, △E, δ T) of several representative luminescent materials.

Materials	Ions	Transitions	ΔE [cm^{-1}]	Max.S_a [$\%K^{-1}$]	Max.S_r [$\%K^{-1}$]	δ T [K]	Ref.
Y2O3	Er^{3+},Yb^{3+}	$^2H_{11/2}$ /$^4S_{3/2}$→$^4I_{15/2}$	791	886/T^2	0.44	1.32	41
Al2O3	Er^{3+},Yb^{3+}	$^2H_{11/2}$ /$^4S_{3/2}$→$^4I_{15/2}$	791	964/T^2	0.51	0.98	43
Y2O3	Tm^{3+},Yb^{3+}	$^1G_{4(1)}$/$^1G_{4(2)}$→$^3H_6$	184	452/T^2	0.35	1.43	58
NaYbF4@SiO2	Tm^{3+}	$^3F_{2,3}$/$^3H_4$→$^3H_6$		2677/T^2	0.054	9.26	61
Y2O_3:	Ho^{3+},Yb^{3+}	$^5F_4$/$^5S_2$→$^5I_8$,$^5I_7$		241/T^2	0.97	0.52	60
$Ba_{0.77}Ca_{0.23}TiO_3$	Ho^{3+},Yb^{3+}	$^5F_4$/$^5S_2$→$^5I_8$,$^5I_7$		182/T^2	1.82	0.27	64

Table S4. Summarized temperature sensing characteristics by using NTCL-FIR temperature sensing method based on Tm^{3+} /Ho^{3+} co-doped different materials in our work.

Materials	I_1/I_2	Transitions	ΔE [cm^{-1}]	Max.S_a [$\%K^{-1}$]	Max.S_r [$\%K^{-1}$]
$YbPO_4$: Tm^{3+}, Ho^{3+}	**700/545**	**$^3F_3 \rightarrow ^3H_6$ (Tm^{3+})/ $^5F_4 \rightarrow ^5I_8$ (Ho^{3+})**	**4102**	**8.58**	**1.99**
	545/476	**$^5F_4 \rightarrow ^5I_8$(Ho^{3+})/ $^1G_4 \rightarrow ^3H_6$ (Tm^{3+})**	**2762**	**0.85**	**1.00**
$NaYb(MoO_4)_2$: Tm^{3+}, Ho^{3+}	**696/545**	**$^3F_3 \rightarrow ^3H_6$ (Tm^{3+})/ $^5F_4 \rightarrow ^5I_8$ (Ho^{3+})**	**4102**	**3.19**	**4.23**
	545/477	**$^5F_4 \rightarrow ^5I_8$(Ho^{3+})/ $^1G_4 \rightarrow ^3H_6$ (Tm^{3+})**	**2762**	**1.95**	**1.40**
$BaTiO_3$: Yb^{3+},Tm^{3+}, Ho^{3+}	**574/478**	**$^5F_4 \rightarrow ^5I_8$(Ho^{3+})/ $^1G_4 \rightarrow ^3H_6$ (Tm^{3+})**	**2762**	**1.92**	**2.95**
$LaAlO_3$: Yb^{3+},Tm^{3+},Ho^{3+}	**545/477**	**$^5F_4 \rightarrow ^5I_8$(Ho^{3+})/ $^1G_4 \rightarrow ^3H_6$ (Tm^{3+})**	**2762**	**7.71**	**1.02**
Y_2O_3: Yb^{3+},Tm^{3+}, Ho^{3+}	**548/485**	**$^5F_4 \rightarrow ^5I_8$(Ho^{3+})/ $^1G_4 \rightarrow ^3H_6$ (Tm^{3+})**	**2762**	**26.99**	**0.65**

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