Supporting Information for

Prediction of Thermal-Coupled Thermometric Performance of Er$^{3+}$

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Experimental section

Synthesis of YAG: 1%Er\(^{3+}\), 3%Yb\(^{3+}\) by the sol-gel method. The rare earth nitrate stock solutions (Y(NO\(_3\))\(_3\) of 0.1 M, Al(NO\(_3\))\(_3\) of 0.5 M, Er(NO\(_3\))\(_3\) of 0.05 M and Yb(NO\(_3\))\(_3\) of 0.1 M) were mixed and stirred in stoichiometric proportions. Then, citric acid, in a molar ratio of [citric acid]/[metals] = 2:1, was dissolved and stirred to transparent solution. The mixed solution was kept at 120 °C for 12 h to generate the gel. The gel was calcined at 500 °C for 2 h and again calcined at 1200 °C for 4 h to obtain the final product.

Synthesis of YbPO\(_4\): 1%Er\(^{3+}\) by the co-precipitation method. Yb(NO\(_3\))\(_3\)·5H\(_2\)O and Er(NO\(_3\))\(_3\)·5H\(_2\)O were dissolved in deionized water in stoichiometric proportions, and the stoichiometric amount of (NH\(_4\))\(_2\)HPO\(_4\) was dissolved in deionized water and dropped into the above solution. After stirring the mixed solution for 7 h, the precipitates were obtained by centrifugation and washed with deionized water and ethanol. The precipitates were dried at 70 °C for 10 h and then calcined at 1200 °C for 2 h to obtain the final product. Synthesis of YPO\(_4\): 1%Er\(^{3+}\), 15%Yb\(^{3+}\) was similar except that Y(NO\(_3\))\(_3\)·5H\(_2\)O was necessary.

Synthesis of LaAlO\(_3\): 1%Er\(^{3+}\), 3%Yb\(^{3+}\) was similar to synthesis of YAG: 1%Er\(^{3+}\), 3%Yb\(^{3+}\). La(NO\(_3\))\(_3\) (0.1 M) and Al(NO\(_3\))\(_3\) (0.5 M) stock solutions were necessary. The final gels were calcined at 500 °C for 2 h and then calcined at 900 °C for 4 h.

Synthesis of Ln\(_2\)O\(_3\): 1%Er\(^{3+}\), 3%Yb\(^{3+}\) (Ln=Lu, Y, Gd and La) by the co-precipitation method. For 1 mmol of Y\(_2\)O\(_3\): 1%Er\(^{3+}\), 3%Yb\(^{3+}\), YCl\(_3\)·6H\(_2\)O, ErCl\(_3\)·6H\(_2\)O and YbCl\(_3\)·6H\(_2\)O were dissolved in 50 mL of deionized water and stirred to transparent. 1.5 g of urea was added and stirred for 30 min. The mixed solution was sealed and kept at 80 °C for 3 h in a water bath. The precursors were collected via centrifugation and washed several times with deionized water. After drying at 70 °C for 10 h, the precursors were calcined at 800 °C for 3 h to yield the final product. The synthesis procedures of Er\(^{3+}/Yb\(^{3+}\) co-doped Lu\(_2\)O\(_3\), Gd\(_2\)O\(_3\) and La\(_2\)O\(_3\) were similar except that the amount of urea for La\(_2\)O\(_3\) was 3 g and LuCl\(_3\)·6H\(_2\)O, GdCl\(_3\)·6H\(_2\)O and LaCl\(_3\)·7H\(_2\)O were necessary.
Synthesis of YVO$_4$: 1%Er$^{3+}$, 15%Yb$^{3+}$ by the hydrothermal method. The rare earth nitrate stock solutions (Y(NO$_3$)$_3$ of 0.1 M, Er(NO$_3$)$_3$ of 0.05 M and Yb(NO$_3$)$_3$ of 0.1 M) were mixed and stirred in stoichiometric proportions. The stoichiometric amount of Na$_3$VO$_4$ was dissolved in appropriate amount of deionized water and dropped into the above solution, and then adjusted the pH value to 10 via the NaOH aqueous solution and stirred for 1 h. Transferred the solution to a Teflon-lined stainless steel autoclave and kept at 200 °C for 16 h. The precipitates were obtained by centrifugation and washed with deionized water and ethanol. After drying at 70 °C for 10 h, the final product was yielded by calcining the precipitates at 600 °C for 2 h. Synthesis of GdVO$_4$: 1%Er$^{3+}$, 15%Yb$^{3+}$ was similar except that Gd(NO$_3$)$_3$ (0.1 M) stock solution was necessary.

**Characterization.**

The crystalline structures of all samples were investigated by X-ray diffraction patterns on a Bruker D8 Focus diffractometer equipped with Cu Kα radiation ($\lambda = 0.15405$ nm). The morphologies were presented via a field emission-scanning electron microscope (FE-SEM, XL30, Philips). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR 27 FT-IR spectrometer. The Luminescence spectra were collected by an Andor SR-500i spectrometer (Andor Technology Co, Belfast, U.K.) equipped with a SR830 DSP lock-in amplifier and a CCD detector under the excitation of a 980 nm diode laser (a spot diameter of 4 mm on the sample). The temperature-dependent spectra were obtained by a copper-constant thermocouple with temperature control system (TAP-02, orient-KOJI).
Figure S1. The XRD patterns, schematic crystal structures and SEM micrographs of Er\(^{3+}/Yb\(^{3+}\) co-doped YAG, YbPO\(_4\), YPO\(_4\), LaAlO\(_3\), Lu\(_2\)O\(_3\), Y\(_2\)O\(_3\), Gd\(_2\)O\(_3\), La\(_2\)O\(_3\), YVO\(_4\) and GdVO\(_4\).
Figure S2. The power-dependent slope factors (n, I~P^n) for the ~525 nm and ~550 nm emissions of Er^{3+}/Yb^{3+} co-doped representative host lattices, indicating the two-photon process of two emissions.
Figure S3. The temperature evolution emission spectra of Er$^{3+}$/Yb$^{3+}$ co-doped diverse host lattices from 313 to 573 K.
Figure S4. The fitting plots of natural logarithm of LIR versus inverse temperature for Er\textsuperscript{3+}/Yb\textsuperscript{3+} co-doped diverse host lattices. Taking the natural logarithm of both sides of Equation 1, the natural logarithm of LIR as a function of inverse temperature is given by

\[
\ln LIR = \ln B - \frac{\Delta E}{K_B T}
\]
Figure S5. The LIR versus T (313–573 K) of Er$^{3+}$/Yb$^{3+}$ co-doped representative host lattices excited by 0.50, 0.75 and 1.00 W.
Figure S6. (a) The XRD patterns, (b) FT-IR spectra, and (c) LIR versus T (313–573 K) of Y₂O₃: 1%Er³⁺, 3%Yb³⁺ sample annealed at 800, 900 and 1000 °C. The increase of the diffraction peaks of XRD patterns indicates that the crystallinity is enhanced. The peak at 564 cm⁻¹ belongs to the stretching vibration of Y–O and has not changed.
Table S1. The Chemical bond parameters of diverse host lattices based on the chemical bond theory of complex crystals.a

<table>
<thead>
<tr>
<th>crystals</th>
<th>nD</th>
<th>bond</th>
<th>αb (Å)</th>
<th>N</th>
<th>αp (Å³)</th>
<th>E_h (eV)</th>
<th>f_i</th>
<th>f_c</th>
<th>Z</th>
<th>K_e</th>
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<tr>
<td>YAG</td>
<td>1.833</td>
<td>Y–O</td>
<td>0.382</td>
<td>8</td>
<td>3.056</td>
<td>4.673</td>
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<td>1.5</td>
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<td>8</td>
<td>3.227</td>
<td>5.059</td>
<td>0.911</td>
<td>0.089</td>
<td>1.125</td>
<td>0.591</td>
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<tr>
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<td>Y–O</td>
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<td>8</td>
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<td>0.089</td>
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<td>La–O</td>
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<td>0.049</td>
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<td>Lu₂O₃</td>
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<td>Lu–O</td>
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<td>6</td>
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<td>Y–O</td>
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<td>La–O(1)</td>
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<td></td>
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<tr>
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a f_c denotes covalency. For La₂O₃, E_h, f_i, f_c and Z take average values and N is total coordination number.
Computational Descriptions

The chemical bond theory of complex structure crystals is an extension of Phillips–Van Vechten–Levine–Tanaka (PVLT) theory, which is used to solve the calculation of multiple bond systems.\(^1\)\(^-\)\(^4\) In a brief description, the structural formula for a complex crystal can be decomposed into the sum of binary crystals as

\[
A_1^i A_2^i A_3^i \ldots A_i^i B_1^j B_2^j B_3^j \ldots B_j^j = \sum_{i,j} A_i^i B_j^j
\]

\[
m_i = \frac{N(B_j^j - A_i^i)a_i}{N_{cA}^i} \quad \text{and} \quad n_j = \frac{N(A_i^i - B_j^j)b_j}{N_{cB}^j}
\]

where A and B represent cations and anions, and \(A_i^i\) and \(B_j^j\) represent the different elements and the element with different sites, and \(a_i\) and \(b_j\) represent the number of the corresponding elements. \(N(B_j^j - A_i^i)\) denotes the number of \(B_j^j\) ions contained in the ligand of the \(A_i^i\) ion, while \(N(A_i^i - B_j^j)\) denotes the opposite. \(N_{cA}^i\) and \(N_{cB}^j\) denote the nearest coordination number of \(A_i^i\) and \(B_j^j\) ions, respectively.

The hosts in this work can be decomposed into the sum of binary crystals according to the crystallographic data as follows

\[
Y_3Al_5O_{12} = Y_3O_6 + Al(l)_{2}O_3 + Al(2)_{3}O_3
\]

\[
YbPO_4 = YbO_{8/3} + PO_{4/3}
\]

\[
YPO_4 = YO_{8/3} + PO_{4/3}
\]

\[
LaAlO_3 = LaO_2 + AlO
\]

\[
Lu_2O_3 = Lu(l)_{3/2}O_{9/4} + Lu(2)_{1/2}O_{3/4}
\]

\[
Y_2O_3 = Y(l)_{3/2}O_{9/4} + Y(2)_{1/2}O_{3/4}
\]

\[
Gd_2O_3 = Gd(l)_{3/2}O_{9/4} + Gd(2)_{1/2}O_{3/4}
\]

\[
La_2O_3 = La_{6/7}O(l) + La_{8/7}O(2)
\]

\[
YVO_4 = YO_{8/3} + VO_{4/3}
\]

\[
GdVO_4 = GdO_{8/3} + VO_{4/3}
\]
Taking YVO$_4$ as an example, each Y atom is surrounded by 8 adjacent O atoms, each V atom has 4 adjacent O atoms, and each O atom is surrounded by 2 Y atoms and 1 V atom. There are 1 Y atom, 1 V atom and 4 O atoms in YVO$_4$. So YVO$_4$ is decomposed into YO$_{8/3}$ and VO$_{4/3}$. Taking La$_2$O$_3$ as another example, O atoms possess two kinds of sites, which are denoted as O(1) and O(2) respectively. Each La atom is surrounded by 3 O(1) atoms and 4 O(2) atoms. Each O(1) atom is surrounded by 6 La atoms and each O(2) atom is surrounded by 4 La atoms. There are 2 La atoms, 1 O(1) atom and 2 O(2) atoms in La$_2$O$_3$. Hence La$_2$O$_3$ is decomposed into La$_{6/7}$O(1) and La$_{8/7}$O(2)$_2$.

Generally, for a binary subformula $A^i_{m}B^j_{n}$ of complex crystals consisting of a variety of cations and one anion, the presenting charge of $A^{(Q_A)}$ is still the normal valence of the cation A, while the presenting charge of B becomes $Q_B^* = m_i Q_A/n_j$. Note that here we only discuss the size of the presenting charge, not including positive and negative properties. Such as Y$_3$Al$_5$O$_{12}$, for Y$_3$O$_6$, $Q_Y = 3$ and $Q_O = 3 \times 3 \times 1/6 = 1.5$ in the Y–O chemical bond. For Al(1)$_2$O$_3$, $Q_{Al} = 3$ and $Q_O = 3 \times 2 \times 1/3 = 2$ in the Al(1)–O chemical bond. For Al(2)$_3$O$_3$, $Q_{Al} = 3$ and $Q_O = 3 \times 3 \times 1/3 = 3$ in the Al(2)–O chemical bond. Gd$_2$O$_3$ has two sites of Gd atoms, where $Q_{{Gd(1)}} = 3$ and $Q_O = 3 \times 3 / 2 \times 4 / 9 = 2$ for Gd(1)$_{3/2}$O$_{9/4}$, $Q_{{Gd(2)}} = 3$ and $Q_O = 3 \times 1 / 2 \times 4 / 3 = 2$ for Gd(1)$_{1/2}$O$_{3/4}$.

The effective valence electrons of any $\mu$-type bond is defined as 

\[
(n_\mu^*) = \frac{(Z_A^\mu)^*}{N_{cA}^\mu} + \frac{(Z_B^\mu)^*}{N_{cB}^\mu}
\]

The effective valence electron density of any $\mu$-type bond is expressed as

\[
(N_e^\mu)^* = \frac{(n_\mu)^*}{v_b^\mu}
\]

where $v_b^\mu$ is the bond volume of any $\mu$-type bond, defined as
Here, $d_v$ is the bond distance (in Å). $N_v^\mu$ is the number of the $\mu$-type bond per cubic centimeter. $\sum$ represents the sum of all types of chemical bonds.

The macroscopic linear susceptibility $\chi$ of crystals can be expressed as

$$\chi = \frac{1 - \varepsilon}{4\pi} = \sum_{\mu} F_{\mu}^\mu \chi_{\mu}^\mu = \sum_{\mu} N_{b}^\mu \chi_{b}^\mu$$

$\varepsilon^\mu$ is the dielectric constant of $\mu$-type bond. $\varepsilon$ is the dielectric constant of crystal, obtained from the refractive index $n$ ($\varepsilon = n^2$). We take $n_D$ (589.3 nm) for different hosts in this work, which is similar to the $n$ values in the luminescent centers (~525 nm and ~550 nm) and easy to obtain. $F^\mu$ is the proportion of $\mu$-type bonds in the total number of chemical bonds of the crystal. $\chi^\mu$ is the total macroscopic susceptibility of $\mu$-type bonds. $N_v^\mu$ is the number of $\mu$-type bonds per cubic centimeter. $\varepsilon^\mu$ is the dielectric constant of $\mu$-type bond. And $\chi_{b}^\mu$ is the susceptibility of a single $\mu$-type bond, expressed as

$$\chi_{b}^\mu = \frac{(\hbar \Omega_{p}^\mu)^2}{4\pi (E_g^\mu)^2}$$

where $E_g^\mu$ is the average energy gap between the bonding molecular orbital and the antibonding molecular orbital of the $\mu$-type bond (in eV). $\Omega_{p}^\mu$ is the plasma frequency, expressed as

$$(\Omega_{p}^\mu)^2 = \frac{4\pi (N_v^\mu)^* e^2}{m D_{\mu} A_{\mu}}$$

$D_{\mu}$ and $A_{\mu}$ are correction factors, expressed as

$$D_{\mu} = \Delta_A^\mu \cdot \Delta_B^\mu - (\delta_A^\mu \cdot \delta_B^\mu - 1) \left[ (Z_A^\mu)^* - (Z_B^\mu)^* \right]^2$$

$$A_{\mu} = 1 - \frac{E_g^\mu}{4E_F^\mu} + \frac{1}{3} \left( \frac{E_g^\mu}{4E_F^\mu} \right)^2$$

where $\Delta$ and $\delta$ are the periodic dependent constants. $E_F^\mu$ is the Fermi energy, expressed
as

\[ E_F^\mu = \frac{(\hbar k_F^\mu)^2}{2m} \]

\[ k_F^\mu = [3\pi^2 (N_c^\mu)^*]^{1/3} \]

\( E_g^\mu \) can be separated into the homopolar energy \( E_h^\mu \) (in eV) and the heteropolar energy \( C^\mu \) (in eV) as follows

\[ (E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \]

The ionicity \( f_i^\mu \) and covalency \( f_c^\mu \) of any \( \mu \)-type bond are defined as follows

\[ f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \quad \text{and} \quad f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2} \]

where

\[ E_g^\mu = \frac{39.74}{(d^\mu)^2.48} \]

\[ C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) [(Z_A^\mu)^* - \frac{n_j}{m_i} (Z_B^\mu)^*] / r_0^\mu \quad (n>m) \]

\[ C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) \frac{m_i}{n_j} (Z_A^\mu)^* - (Z_B^\mu)^*] / r_0^\mu \quad (n<m) \]

\[ k_s^\mu = (4k_F^\mu / \pi a_B)^{1/2} \]

\[ r_0^\mu = d^\mu / 2 \]

Here, \( a_B \) is the Bohr radius. \( \exp(-k_s^\mu r_0^\mu) \) is the Thomas-Fermi screening factor. \( b^\mu \) is the structural correction factor, which is related to the average coordination number \( N_c^\mu \) and is expressed as follows

\[ b^\mu = \beta (N_c^\mu)^p \]

\[ N_c^\mu = \frac{m_i}{m_i + n_j} N_c^\mu_{cA} + \frac{n_j}{m_i + n_j} N_c^\mu_{cB} \]

The polarizable coefficient \( a_{\mu}^p \) of the \( \mu \)-type bond can be derived from the Lorentz-Lorenz equation as follows
\[ \varepsilon^\mu - 1 = \frac{4}{3} \mu a_0^\mu \]

The polarizability of the chemical bond volume is expressed as

\[ a_b^\mu = a_0^\mu V_b^\mu \]

Note that when calculating \( K_e \) for La\(_2\)O\(_3\), the \( E_b, f_i, f_c \) and \( Z \) parameters of La–O(1) and La–O(2) chemical bonds are calculated first, and then the average values are taken.

References


(5) Zelmon, D. E.; Small, D. L.; Page, R. Refractive-Index Measurements of Undoped Yttrium Aluminum Garnet from 0.4 to 5.0 \( \mu \)m. *Appl. Optics* 1998, 37, 4933-4935.


