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Boltzmann luminescent nanothermometry: mechanistic criteria and predictive design of thermally coupled levels

Kejie Li¹, Jiaqi Zhao¹, Mochen Jia²✉, Dongxu Guo¹, Ruiying Lu¹, Zhiying Wang³✉ and Zuoling Fu¹✉

Abstract

Boltzmann-type luminescent nanothermometry using thermally coupled levels (TCLs) of lanthanide ions is promising for applications in nanotechnology, biomedicine, and aerospace. However, the fundamental rules governing TCLs formation and the reliable prediction of relative sensitivity (S_r) in specific hosts remain unclear. Here, we develop a population-dynamics framework that quantitatively defines the onset temperature and the thermal coupling window for Boltzmann behavior, dictated by nonradiative rates and the thermalization energy gap (ΔE). Mechanistic analysis reveals how adjacent levels disturb the balance between thermal population and multi-phonon relaxation, and establishes a practical stability criterion: robust coupling occurs when the nearest lower level lies beyond $2\Delta E$. To enable predictive thermometric design, we introduce a splitting factor that correlates macroscopic S_r with microscopic chemical bond parameters. Leveraging two TCLs pairs, we further demonstrate ultrathin, flexible thermosensing patches with high brightness and S_r up to $6.17\% \text{ K}^{-1}$, enabling real-time in situ temperature mapping during reactions. This work provides physics-based guidelines for the rational design of high-precision luminescent nanothermometers.

Introduction

Luminescent nanothermometry has emerged as a versatile platform for remote and non-invasive temperature sensing, in which thermal information is transduced into optical signals^{1–5}. Compared with conventional electronic probes, luminescence-based thermometers enable remote operation, high spatial resolution, and fast readout, making them particularly attractive for applications ranging from nanotechnology and biomedicine to aerospace engineering^{6–9}. Among the various optical strategies, ratiometric nanothermometry based on thermally coupled levels (TCLs) of lanthanide ions is especially appealing^{10,11}. The relative population of two close-lying excited states follows a Boltzmann distribution, such that their emission intensity ratio provides a self-referenced and calibration-stable measure of temperature. This approach

promises high accuracy and robustness against fluctuations in excitation intensity or probe concentration^{12,13}. By combining safety, sensitivity, and reliability, TCL-based nanothermometry has been advanced toward demanding applications, ranging from probing the thermophysical properties of nanofluids and elucidating heat-generation mechanisms in lithium-ion batteries to real-time in situ temperature feedback during cellular and tissue thermal therapies^{14–16}.

Despite their potential, the theoretical understanding and predictive design of TCL-based luminescent thermometers remain incomplete. In practice, many nominally “Boltzmann-type” two-level systems exhibit significant deviations from the ideal law. Experimental luminescence intensity ratios (LIRs) often diverge from the expected Boltzmann dependence due to incomplete thermalization, parasitic nonradiative processes, or interactions with adjacent electronic states^{17–20}. Such effects can lead to calibration inconsistencies, with the same lanthanide-host combination yielding disparate sensitivity values or effective energy gaps across different studies. For example, sluggish multi-phonon relaxation can prevent

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thermal equilibrium between the two levels, while nearby states may couple to the TCLs pair and distort the population dynamics. These uncertainties highlight the lack of mechanistic criteria for establishing when a TCL-based system will exhibit reliable Boltzmann behavior, and why certain hosts deliver superior thermal sensitivities compared to others²¹. As a result, the design of high-performance nanothermometers has remained largely empirical, constrained by the lack of a quantitative framework that defines the thermal coupling behavior and links microscopic material parameters to macroscopic thermometric performance.

Here, we address these fundamental limitations by establishing a population-dynamics framework that quantitatively defines the onset temperature and the operational window for ideal Boltzmann behavior in TCLs. Our mechanistic investigation reveals how adjacent energy levels disrupt the equilibrium between thermal population and multi-phonon relaxation, leading to a practical criterion for stable thermal coupling. Furthermore, we introduce a splitting factor to bridge the macroscopic relative sensitivity (S_r) with microscopic chemical bond parameters, enabling a predictable design strategy. To demonstrate the practical utility of our model, we engineered high-brightness, ultrathin, and flexible thermosensing patches utilizing two pairs of TCLs, achieving a high S_r of up to 6.17% K⁻¹ for real-time in situ temperature monitoring. This work provides physics-based guidelines for the rational design of high-precision luminescent nanothermometers, moving beyond trial-and-error approaches.

Results

TCL-based design

For two thermally coupled levels (TCLs) of the same lanthanide ion, their relative populations approach quasi-thermal equilibrium following the Boltzmann distribution. This condition is typically satisfied when the energy gap (ΔE) between the two levels falls within 200–2000 cm⁻¹ (ref.²²). With rising temperature, thermal excitation promotes electron transitions from the lower state (L_1) to the higher state (L_2), producing a temperature-dependent change in the emission intensity ratio between $L_2 \rightarrow L_0$ and $L_1 \rightarrow L_0$ transitions, where L_0 denotes the ground state. Based on the Boltzmann distribution, the luminescence intensity ratio (LIR) can be expressed as²³:

$$\text{LIR} = \frac{I(L_2)}{I(L_1)} = \frac{N_2 h \omega_2 A_2}{N_1 h \omega_1 A_1} = \frac{g_2 \omega_2 A_2}{g_1 \omega_1 A_1} \exp\left(\frac{-\Delta E}{k_B T}\right) = B \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (1)$$

with $B = \frac{g_2 \omega_2 A_2}{g_1 \omega_1 A_1}$

where N , A , and ω represent the electron population, spontaneous emission rate, and emission angular frequency,

respectively, g is the degeneracy, and h and k_B denote Planck's and Boltzmann's constants. Taken together with Eqs. (1) and (S1), this indicates a positive correlation between relative sensitivity (S_r) and ΔE ²⁴ (Supplementary Note 2). As depicted in Fig. 1a, representative TCLs of lanthanide ions (Ln³⁺) span from ultraviolet (UV) to near-infrared (NIR) regions, enabling tailored selection for specific applications. In the short-wavelength UV region, Gd³⁺ (⁶P_{3/2}, ⁶P_{5/2}, ⁶P_{7/2}) provides exceptional resistance to electromagnetic interference and strong plasma penetration. In the visible region, emissions from Ho³⁺ (⁵F₁, ⁵F₂, ⁵F₃), Er³⁺ (²H_{11/2}, ⁴S_{3/2}), Pr³⁺ (³P₁, ³P₀), Eu³⁺ (⁵D₁, ⁵D₀), and Sm³⁺ (⁴F_{3/2}, ⁴G_{5/2}) enable direct optical detection, making these ions particularly suitable for cell labeling. In the first biological window (NIR-I, 700–900 nm), Nd³⁺ (⁴F_{7/2}, ⁴F_{5/2}, ⁴F_{3/2}) and Tm³⁺ (³F₃, ³H₄) facilitate deep-tissue imaging and photothermal therapy. Yb³⁺ (²F_{5/2}) and Er³⁺ (⁴I_{13/2}), emitting in the NIR-II region (1000–1700 nm), provide low scattering and high signal-to-noise ratios, significantly benefiting in vivo imaging. Although Fig. 1b outlines ideal ΔE values between TCLs, practical deviations commonly arise from host-matrix effects. The relationship between S_r and temperature for various ΔE values is demonstrated in Fig. S1, highlighting ΔE as a primary design parameter.

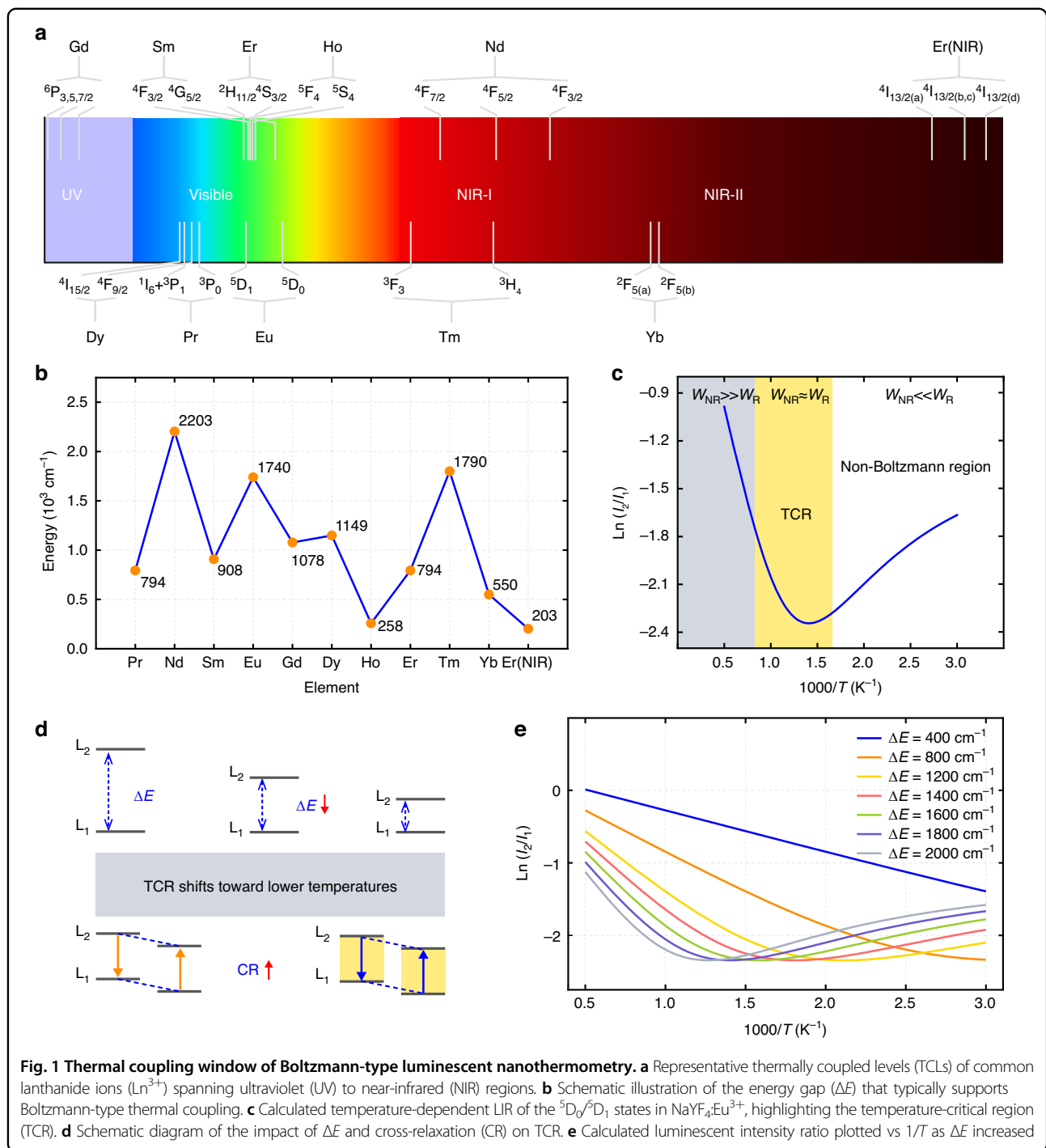
Building on this overview, the following rate-equation model formalizes the temperature-dependent behavior. Coupled rate equations were established for the populations of the TCLs L_1 and L_2 , N_1 and N_2 , under idealized conditions in which all photoexcited carriers are rapidly funneled into the TCLs and exclusively populate L_1 and L_2 , whereas energy transfer, energy migration, and concentration quenching are neglected:

$$\frac{dN_1}{dt} = \beta_{\text{up} \rightarrow 1} N_{\text{up}} - \frac{N_1}{\tau_1} + M\rho[(1+n)^p g_1 N_2 - n^p g_2 N_1] \quad (2)$$

$$\frac{dN_2}{dt} = \beta_{\text{up} \rightarrow 2} N_{\text{up}} - \frac{N_2}{\tau_2} - M\rho[(1+n)^p g_1 N_2 - n^p g_2 N_1] \quad (3)$$

where N_{up} denotes the population initially promoted to higher-lying states; $\beta_{\text{up} \rightarrow 1}$ and $\beta_{\text{up} \rightarrow 2}$ are the branching fractions for relaxation from N_{up} into L_1 and L_2 , respectively, with $\beta_{\text{up} \rightarrow 1} + \beta_{\text{up} \rightarrow 2} = 1$. Radiative relaxation from level L_i is represented by N_i/τ_i , where τ_i is the radiative lifetime. Bidirectional multiphonon relaxation between L_1 and L_2 proceeds with rates proportional to $M\rho$ (the product of the net interaction matrix element and the phonon density of states at the relevant frequency) and to the level degeneracy g_i . Pairing the





degeneracy factors with the opposite-level populations (g_1 with N_2 and g_2 with N_1) enforces detailed balance, ensuring that when thermal relaxation dominates, the populations follow Boltzmann statistics. The multiphonon relaxation rate varies exponentially with p , the number of phonons required to bridge ΔE . The phonon-emission rate is proportional to $(n+1)^p$, while the phonon-absorption rate is proportional to n^p ,

where n is the Bose-Einstein phonon occupation number^{25,26}:

$$n = \frac{1}{\exp\left(\frac{\Delta E}{pk_B T}\right) - 1} \quad (4)$$

Within this framework, the temperature dependence of the LIR under continuous-wave excitation was quantified.

Under steady-state conditions, N_1 and N_2 become time-invariant. The coupled rate equations were solved in matrix form:

$$\begin{pmatrix} \frac{1}{\tau_1} + M\rho g_2 n^p & -M\rho g_1(1+n)^p \\ -M\rho g_2 n^p & \frac{1}{\tau_2} + M\rho g_1(1+n)^p \end{pmatrix} \begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = \begin{pmatrix} \beta_{\text{up} \rightarrow 1} N_{\text{up}} \\ \beta_{\text{up} \rightarrow 2} N_{\text{up}} \end{pmatrix} \quad (5)$$

Because the radiative lifetimes of the TCLs are nearly identical and are fixed to a common value (i.e., $\tau_1 = \tau_2 = \tau_R$), yielding the LIR expression:

$$\frac{I_2}{I_1} = C \frac{\frac{\beta_{\text{up} \rightarrow 2}}{\tau_R} + M\rho g_2 n^p}{\frac{\beta_{\text{up} \rightarrow 1}}{\tau_R} + M\rho g_1(1+n)n^p} \quad (6)$$

Using the $^5\text{D}_0$ and $^5\text{D}_1$ states of $\text{NaYF}_4:\text{Eu}^{3+}$ as a model (detailed values in Table S1)²⁷, the calculated I_2/I_1 versus temperature is shown in Fig. 1c. The temperature-critical region (TCR) is defined as the regime in which the nonradiative relaxation rate is comparable to the radiative decay rate. The nonradiative and radiative relaxation rates are defined as²⁷:

$$W_{\text{NR}} = \frac{1}{\tau_{\text{NR}}} = M\rho[(1+n)^p g_1 + n^p g_2] \quad (7)$$

$$W_{\text{R}} = \frac{1}{\tau_{\text{R}}} \quad (8)$$

Below the TCR, $W_{\text{R}} \gg W_{\text{NR}}$, thermal equilibration between the two levels is not established, and the LIR deviates from the Boltzmann law. Once the temperature exceeds the TCR, $W_{\text{NR}} \gg W_{\text{R}}$, interlevel exchange becomes rapid, and the LIR-temperature relation follows Boltzmann behavior²⁸. ΔE plays a pivotal role in setting the TCR (Fig. 1d). For rare-earth $4f4f$ transitions, the energy-gap law states that the nonradiative multiphonon rate decreases exponentially with increasing level separation ΔE ^{29,30}:

$$W_{\text{NR}}(\Delta E) \approx W_0 \exp(-\gamma \Delta E) \quad (9)$$

where W_{NR} denotes the nonradiative rate and W_0 is the intrinsic nonradiative rate. γ is governed primarily by the host's maximum effective phonon energy and the strength of electron-phonon coupling, and an approximate value of 0.00314 cm^{-1} is adopted³¹. Accordingly, ΔE was scanned from 200 to 2000 cm^{-1} to simulate the temperature dependence of I_2/I_1 . As shown in Fig. 1e, when $\Delta E = 2000 \text{ cm}^{-1}$, the minimum temperature required to establish Boltzmann equilibrium under ideal conditions is about 1000 K, which motivates our practical constraint that the TCLs separation be kept within 2000 cm^{-1} . As ΔE decreases, the TCR shifts to lower temperatures, indicating a reduced threshold for achieving Boltzmann equilibrium.

Likewise, at fixed ΔE , increasing the dopant concentration enhances cross-relaxation between the levels, raises W_{NR} , and shifts the TCR toward lower temperatures (Fig. 1d).

However, for most lanthanide ion pairs with ΔE in the range of $200\text{--}2000 \text{ cm}^{-1}$, the dependence of the LIR on temperature deviates from Boltzmann behavior over a substantial temperature interval. The Boltzmann distribution gives the probability that particles occupy different energy levels in a system at thermal equilibrium (Supplementary Note 3). It applies to the canonical ensemble: the particle number N is fixed, the system can exchange energy with a heat bath, and particle exchange is forbidden³². TCLs are not isolated, closed systems. Under ideal conditions, carriers promoted to an upper manifold relax rapidly into L_1 and L_2 and reach thermal equilibrium on a sub-millisecond timescale. A critical but often overlooked factor is the coupling to the nearest lower-lying level, denoted L_{lower} . As shown in Fig. 2a, TCLs commonly used for LIR thermometry were surveyed, and the energy offset ΔE_{lower} between the lower TCL state L_1 and the nearest lower-lying level L_{lower} was compiled. The specific energy-level assignments of L_1 , L_2 , and L_{lower} for each Ln^{3+} , together with their corresponding wave-numbers, are summarized in Supplementary Table S2. A consistent trend emerges: ΔE_{lower} is greater than, and often far greater than, 2000 cm^{-1} . For representative ions such as Eu^{3+} and Gd^{3+} , the values extend beyond 10^4 cm^{-1} . The ratios $\Delta E_{\text{lower}}/\Delta E$, listed with each entry, span from 2.35 for Nd^{3+} to 30.69 for Er^{3+} . These data indicate that ΔE_{lower} must substantially exceed ΔE for the LIR-temperature relation to follow Boltzmann statistics.

Motivated by this discrepancy, we introduced a virtual level below L_1 (Fig. 2b) to quantify the specific impact of L_{lower} , and added L_{lower} correction terms to the differential equations for the ideal level populations N_1 and N_2 :

$$\frac{dN_1}{dt} = \beta_{\text{up} \rightarrow 1} N_{\text{up}} - \frac{N_1}{\tau_1} + M\rho[(1+n)^p g_1 N_2 - n^p g_2 N_1] - X_2 N_1 \quad (10)$$

$$\frac{dN_2}{dt} = \beta_{\text{up} \rightarrow 2} N_{\text{up}} - \frac{N_2}{\tau_2} - M\rho[(1+n)^p g_1 N_2 - n^p g_2 N_1] - X_1 N_2 \quad (11)$$

where X_2 and X_1 denote the nonradiative relaxation rates from $L_2 \rightarrow L_{\text{lower}}$ and $L_1 \rightarrow L_{\text{lower}}$, respectively. In the model, both rates obey the energy-gap law. Under continuous-wave excitation, the system is solved in the steady state:

$$\frac{I_2}{I_1} = C \frac{\beta_{\text{up} \rightarrow 2}(\frac{1}{\tau_R} + X_2) + M\rho g_2 n^p}{\beta_{\text{up} \rightarrow 1}(\frac{1}{\tau_R} + X_1) + M\rho g_1(1+n)n^p} \quad (12)$$

We simulated cases with ΔE_{lower} set to 0.1–3.0 times ΔE . The resulting I_2/I_1 -temperature curves are shown in



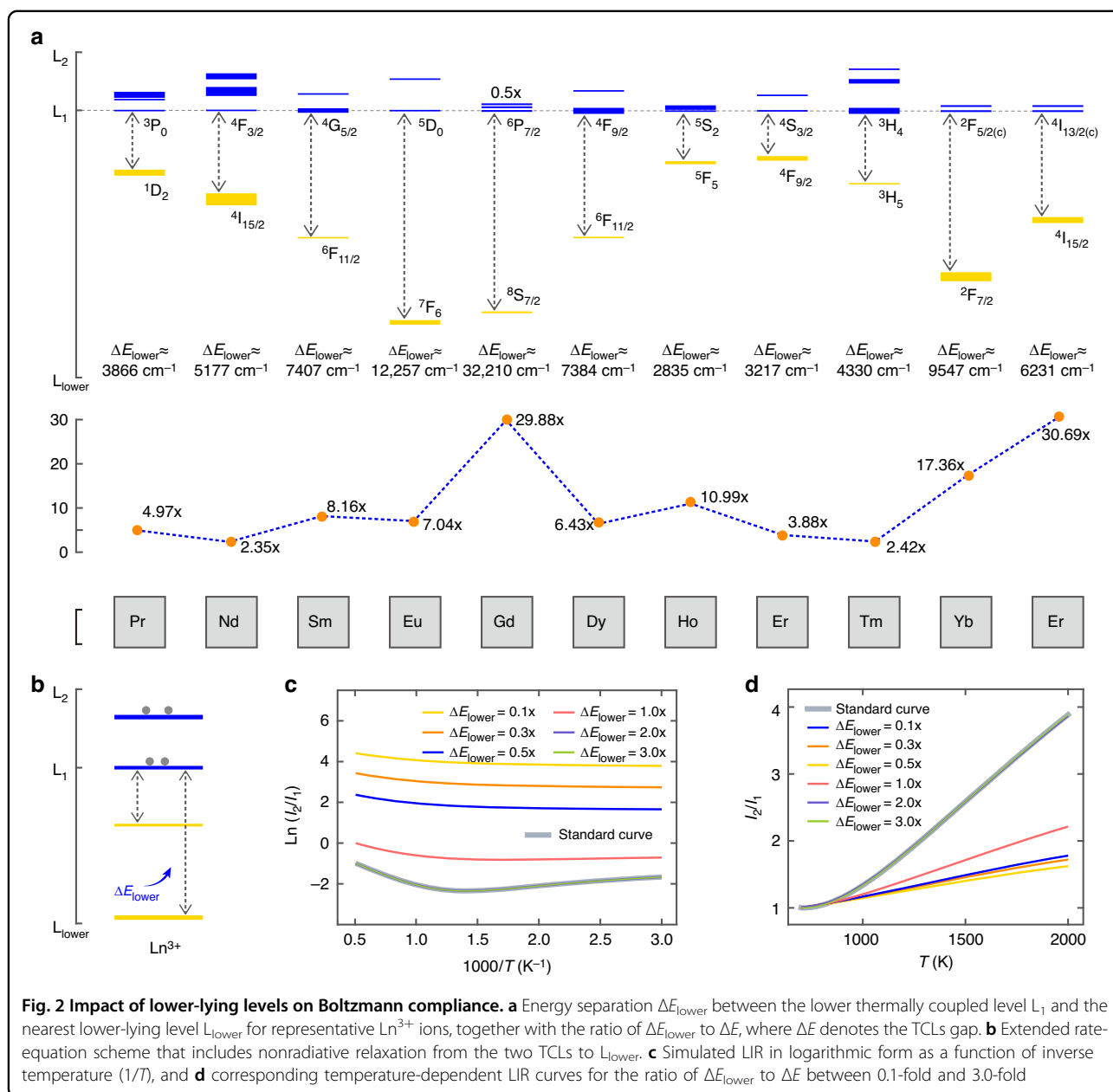


Fig. 2 Impact of lower-lying levels on Boltzmann compliance. **a** Energy separation ΔE_{lower} between the lower thermally coupled level L_1 and the nearest lower-lying level L_{lower} for representative Ln^{3+} ions, together with the ratio of ΔE_{lower} to ΔE , where ΔE denotes the TCLs gap. **b** Extended rate equation scheme that includes nonradiative relaxation from the two TCLs to L_{lower} . **c** Simulated LIR in logarithmic form as a function of inverse temperature ($1/T$), and **d** corresponding temperature-dependent LIR curves for the ratio of ΔE_{lower} to ΔE between 0.1-fold and 3.0-fold

Fig. 2c. When ΔE_{lower} is no more than twice ΔE , the I_2/I_1 response deviates markedly from the ideal Boltzmann reference. After normalizing I_2/I_1 at the TCR, Fig. 2d shows a clear trend: smaller $\Delta E_{\text{lower}}/\Delta E$ ratios produce increasingly pronounced departures from the Boltzmann curve. The deviation is most severe at $\Delta E_{\text{lower}} = 0.1\Delta E$, where the response becomes nearly linear. By contrast, when $\Delta E_{\text{lower}} \geq 2\Delta E$, the calculated I_2/I_1 curve almost fully overlaps the ideal reference, indicating that the lower-lying level no longer perturbs the TCLs population distribution. These results rationalize why energy-level pairs of Ln^{3+} ions with ΔE in the 200–2000 cm^{-1} range often fail to deliver reliable TCL-based thermometry, and they

provide practical guidance for engineering high-performance TCLs thermometers that have not yet been realized.

Having established the role of L_{lower} , we next considered host-imposed constraints on ΔE and S_r . Within a given host lattice, ΔE values between TCLs generally fall within a relatively fixed interval. For example, systematic measurements of the ΔE between $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels of Er^{3+} across a variety of hosts are collected in Supplementary Note 4. Comprehensive analyzes based on chemical bond theory of dielectric description reveal a strong correlation between ΔE and microscopic crystal-field parameters. On this basis, a quantitative model was

formulated that links ΔE to the energy-level splitting factor K_e , thereby establishing an explicit relationship between the S_r and K_e ³³:

$$S_r = \frac{\Delta E}{k_B T^2} = \frac{1000.10 - 180.03 K_e^{-0.5}}{k_B T^2} \quad (13)$$

with $K_e = \frac{E_h Z f_i^2}{N}$

where E_h and f_i denote, respectively, the mean homopolar bond energy and the average bond ionicity for the lanthanide-ligand interaction, and Z is the mean effective charge carried by the ligands, with N being the nearest-neighbor coordination number. This theory was subsequently extended to fluorides, with detailed calculations provided in the Supplementary Note 4. To validate the model experimentally, temperature-dependent upconversion (UC) spectra of $\text{LiYF}_4: \text{Yb}^{3+}, \text{Er}^{3+}$ under 980 nm excitation were recorded (Figs. S2 and S3). At 313 K, the maximum S_r reached 1.14% K^{-1} , and the experimentally extracted ΔE agreed closely with the model prediction ($K_e = 0.630$). A similar performance was observed for fluoride double perovskites. The composition $\text{Cs}_2\text{NaYF}_6: 4\%\text{Yb}^{3+}, 6\%\text{Er}^{3+}$ delivered an S_r of 1.14% K^{-1} at 313 K (Figs. S4–S7), with the measured ΔE lying near the fitted curve ($K_e = 0.686$). These results indicate that host-determined intrinsic ΔE provides a primary criterion for material selection and sets the theoretical ceiling for S_r , thereby defining a fundamental limitation for further improvements in TCL-based temperature sensing.

To overcome these host-imposed limits, we next investigated deliberate crystal-field engineering to relax this host constraint. For the transitions from L_1 and L_2 to L_0 , energy level splitting induced a shift in the barycenter of the emission spectra, consequently enlarging ΔE between the TCLs (Fig. 3a). The host lattice of $\text{Cs}_2\text{NaYF}_6: 4\%\text{Yb}^{3+}, 6\%\text{Er}^{3+}$ was crystallized in the cubic space group Fm-3m , characterized by high symmetry with O_h point group symmetry. Within this centrosymmetric environment, $4f-4f$ transitions of rare-earth ions were generally electric-dipole forbidden due to the identical parity of $4f^n$ configurations, causing negligible transition dipole moments³⁴. To overcome this limitation, lattice distortion was induced by co-doping with Li^+ (Supplementary Note 5). At an optimized doping concentration of 2% Li^+ , the emission intensity of Er^{3+} TCLs ($^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$) reached its maximum (Fig. S8). Structural analysis confirmed that the incorporation of Li^+ ions distorted the $[\text{YF}_6]^{3-}$ octahedra, effectively lifting the parity-forbidden selection rules and substantially enhancing the stiffness of the host lattice (Supplementary Note 6). Crystal field modulation maximized Stark splitting of the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels into four and one sublevel, respectively, as verified by irreducible

representation analysis based on O_h point group symmetry (Supplementary Note 7). Based on emission barycenter calculations³⁵ (Supplementary Note 8), co-doping 2% Li^+ into $\text{Cs}_2\text{NaYF}_6: 4\%\text{Yb}^{3+}, 6\%\text{Er}^{3+}$ increases the gap ΔE between the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels by $\approx 200 \text{ cm}^{-1}$ relative to $\text{Cs}_2\text{NaYF}_6: 4\%\text{Yb}^{3+}, 6\%\text{Er}^{3+}$ (Fig. 3b), indicating a substantial boost in the S_r for TCL-based thermometry. As shown in Fig. 3c, the Stark sublevels of $^2\text{H}_{11/2}$ are labeled X_1 – X_4 . The lowest sublevel X_1 serves as the acceptor state, which reduces the minimum gap $\Delta E_{\min}$ between $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$, accelerates the nonradiative $^2\text{H}_{11/2}$ to $^4\text{S}_{3/2}$ channel, and thereby strengthens thermal coupling. This is corroborated by an increase in the emission-intensity ratio $I(^4\text{S}_{3/2})/I(^2\text{H}_{11/2})$ (Fig. 3b). Conversely, the presence of the highest Stark sublevel X_4 increases the maximum gap $\Delta E_{\max}$, and thermal coupling among X_1 – X_4 drives population toward X_4 , shifting the $^2\text{H}_{11/2}$ emission barycenter to higher energy and raising the overall ΔE . Consistent with these effects, S_r increases from 1.14% to 1.27% K^{-1} upon 2% Li^+ co-doping (Figs. 3d and S9), surpassing the predicted host-imposed limit for Cs_2NaYF_6 (Fig. 3e) and thereby relaxing the matrix constraint on S_r .

Combined two TCLs

Conventional ratiometric thermometry relies on a single pair of TCLs, where the S_r is fundamentally limited by the intrinsic energy separation. To further enhance thermometric performance, we integrated two distinct TCLs by pairing one emission exhibiting the strongest thermal enhancement with another showing the most pronounced thermal quenching (Fig. 4a). This complementary design maximizes the contrast in thermal response, thereby amplifying the intensity ratio variation with temperature (Fig. 4b). When the separation between two distinct TCLs is at least twice each pair's own interlevel gap, their mutual perturbation can be neglected. In most cases, the temperature dependence of the emission intensity ratio between two levels can be written as:

$$\text{LIR} = \frac{I_1(T)}{I_2(T)} = a + b \exp\left(\frac{c}{T}\right) \quad (14)$$

The S_r is further derived as:

$$S_r = \left| \frac{1}{\text{LIR}} \frac{\partial \text{LIR}}{\partial T} \right| = \left| \frac{bc \exp(\frac{c}{T})}{T^2 [a + b \exp(\frac{c}{T})]} \right| \quad (15)$$

To examine the sensitivity of S_r to each parameter, a , b , and c are assumed positive. When $b \exp(c/T) \gg a$, the denominator approximates $b \exp(c/T)$, yielding $S_r \approx c/T^2$, indicating insensitivity to parameter b . When $b \exp(c/T) \ll a$, the denominator approaches a , making S_r



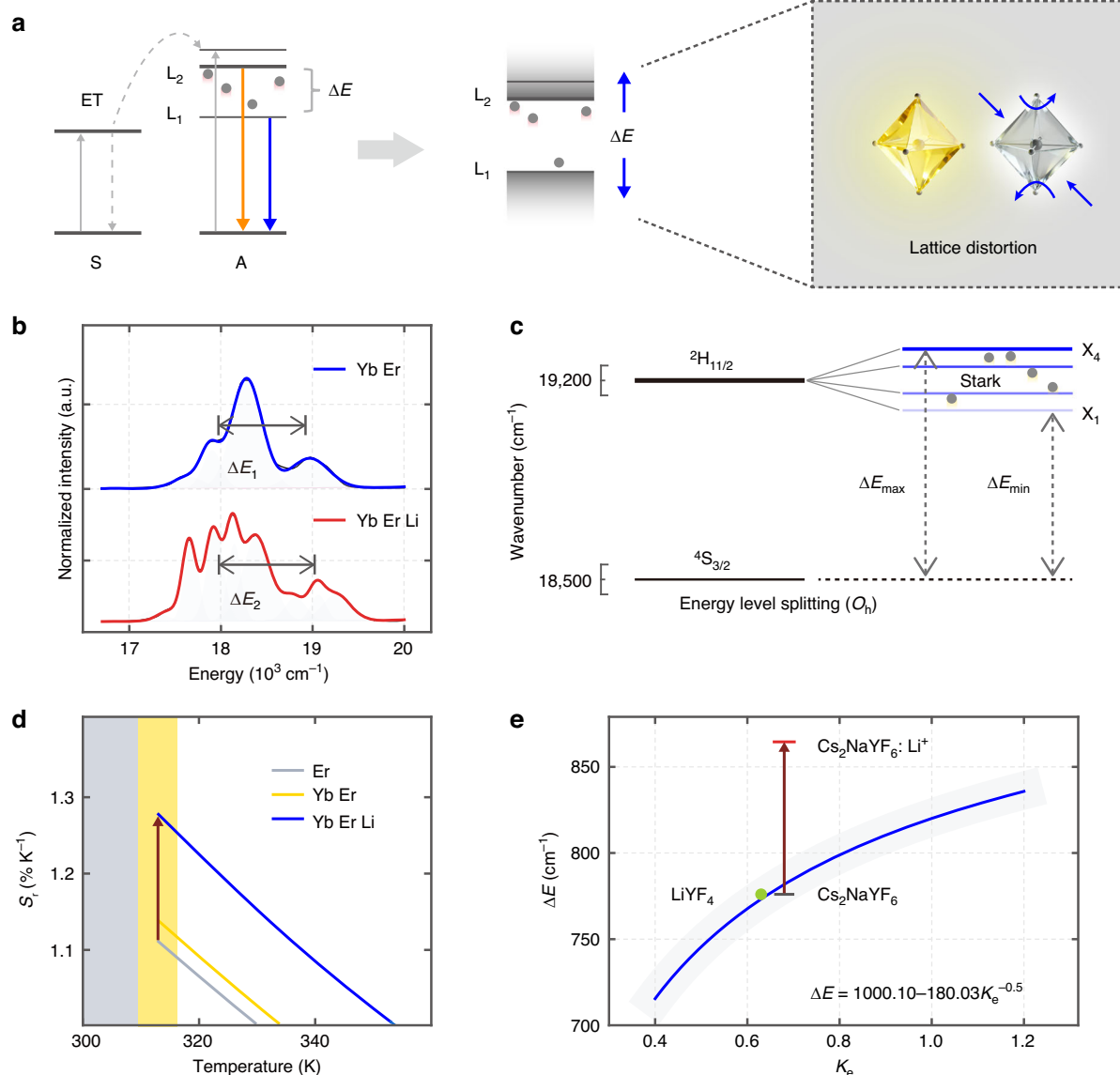


Fig. 3 Crystal-field engineering and prediction of thermally coupled thermometric performance. **a** Schematic illustration of emission barycenter shifts caused by crystal-field splitting. **b** Emission spectra of $\text{Cs}_2\text{NaYF}_6: 4\%\text{Yb}^{3+}, 6\%\text{Er}^{3+}$ with and without 2% Li^+ co-doping under 980 nm excitation. Gaussian fits are used to obtain emission barycenters of the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, from which ΔE is calculated. **c** Energy level splitting of thermally coupled levels ($^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$) under O_h symmetry. **d** S_r ($^2\text{H}_{11/2}/^4\text{S}_{3/2}$) increased with the ΔE expansion. **e** Comparison of experimentally extracted ΔE values and model predictions across different fluoride hosts. Li^+ co-doping in Cs_2NaYF_6 surpasses the host-imposed limit, demonstrating relaxation of the intrinsic matrix constraint on S_r .

proportional to b , thus demonstrating sensitivity to b . Parameter c exerts a dual influence, appearing linearly in the numerator and exponentially in the exponential term, resulting in $S_r \propto c \exp(c/T)$. Consequently, S_r is highly sensitive to c , particularly at high c/T values, where the exponential term dominates and further amplifies the impact of c . Conversely, parameter a has minimal influence, appearing merely as an additive term in the denominator. Notably, when $b \exp(c/T) \gg a$, the contribution of a to S_r becomes negligible, establishing c as

the primary determinant of sensitivity. As shown in Figs. S10 and S11, variations in a and b produce minimal changes in S_r , whereas increasing c significantly enhances S_r . In Supplementary Note 9, we establish a temperature-dependent model for Ln^{3+} emission intensity, $c = -E_{\text{equ}}/k_B$, where E_{equ} is the equivalent (or dominant) approximate energy associated with thermally activated enhancement channels and nonradiative quenching pathways^{36,37}. This substantiates the strategy of pairing the emission that exhibits the strongest thermal



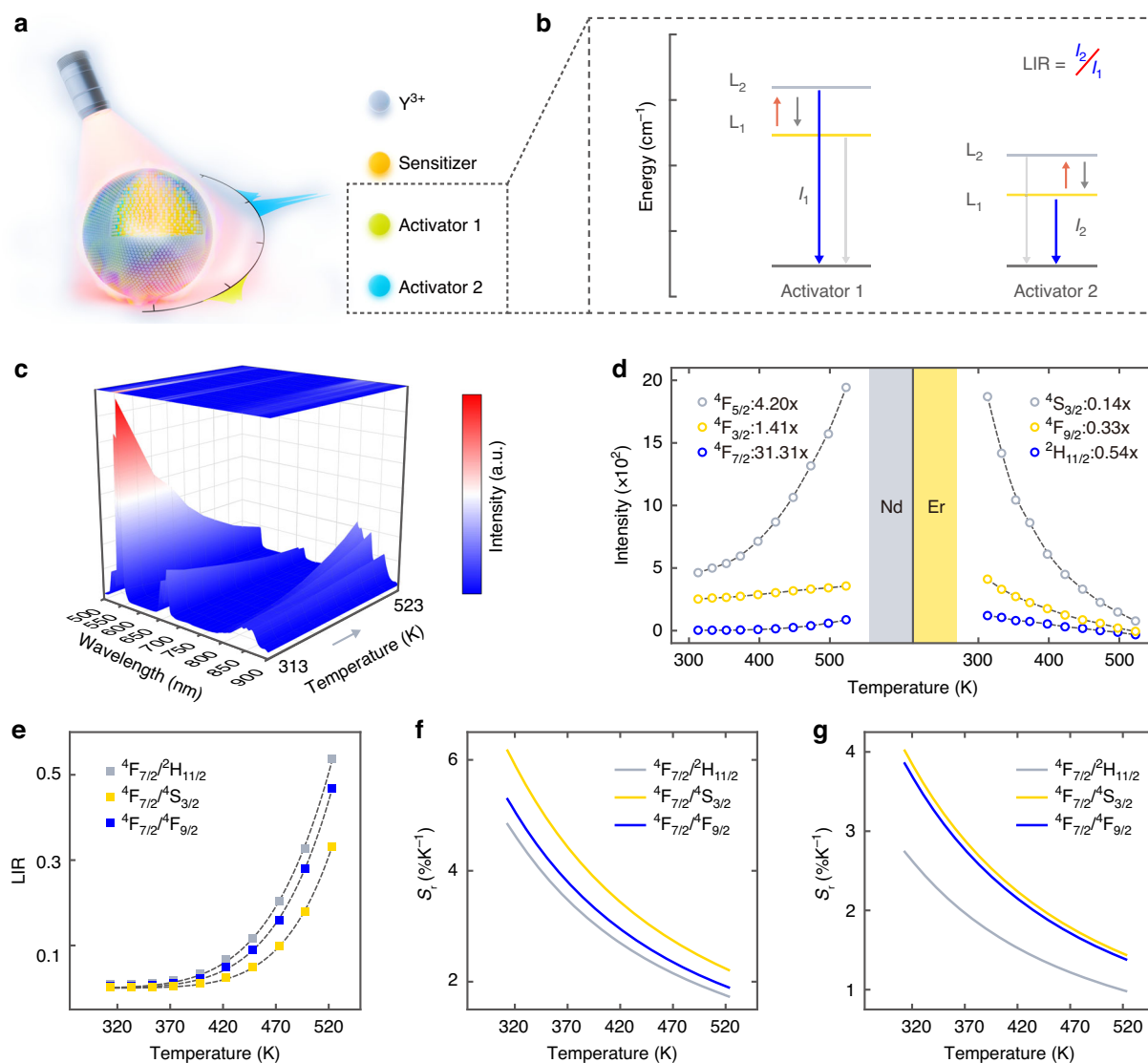


Fig. 4 High-sensitivity ratiometric thermometry by combining two pairs of thermally coupled levels. **a** Schematic of a dual-emitter system co-doped with a sensitizer and two distinct activators. **b** Schematic representation of the combination of two pairs of TCLs. **c** Temperature-dependent photoluminescence (PL) spectra of LiYF_4 : 20% Yb^{3+} , 5% Nd^{3+} , 2% Er^{3+} under 980 nm excitation. **d** Integrated luminescent intensities of representative Er^{3+} and Nd^{3+} transitions as a function of temperature. **e** LIR and **f** S_r ($^4\text{F}_{7/2}/^2\text{H}_{11/2}$, $^4\text{F}_{7/2}/^4\text{S}_{3/2}$ and $^4\text{F}_{7/2}/^4\text{F}_{9/2}$) versus temperature for LiYF_4 : 20% Yb^{3+} , 5% Nd^{3+} , 2% Er^{3+} . **g** S_r ($^4\text{F}_{7/2}/^2\text{H}_{11/2}$, $^4\text{F}_{7/2}/^4\text{S}_{3/2}$ and $^4\text{F}_{7/2}/^4\text{F}_{9/2}$) versus temperature for Cs_2NaYF_6 : 4% Yb^{3+} , 4% Nd^{3+} , 2% Er^{3+} , 2% Li^{+}

enhancement with the emission that undergoes the most pronounced thermal quenching, thereby maximizing the differential response and increasing S_r .

Guided by the above criteria, Er^{3+} and Nd^{3+} provide a representative case. For Er^{3+} , the transitions $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ undergo conventional thermal quenching, with $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (lower TCL, L_1) quenching more severely due to thermal coupling. In contrast, Nd^{3+} emissions from $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{5/2} \rightarrow ^4\text{I}_{9/2}$, and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ exhibit strong thermal enhancement under thermal coupling. The energy separations between these levels

range from 5002 to 7999 cm^{-1} , exceeding $2\Delta E$ (Er) and $2\Delta E$ (Nd), where ΔE (Er) denotes the TCLs gap between the Er^{3+} levels $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$, and ΔE (Nd) denotes that between the Nd^{3+} levels $^4\text{F}_{7/2}$ and $^4\text{F}_{3/2}$. Such a large separation suggests mutual independence with minimal spectral overlap, rendering this pair well-suited for high-sensitivity thermometry in a dual-TCL architecture.

With this rationale in mind, Nd^{3+} was first introduced into LiYF_4 together with Yb^{3+} as a sensitizer (Fig. S12). Under 980 nm excitation, the $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{5/2} \rightarrow ^4\text{I}_{9/2}$, and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions of Nd^{3+} exhibit thermal



enhancement, attributable to phonon-assisted $\text{Yb}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer and thermal coupling between the ground and first excited manifolds of Nd^{3+} (Fig. S13). The LIRs (${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$) and (${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$) were fitted using Eq. (1), yielding maximum S_r values of $1.61\% \text{ K}^{-1}$ for ${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$ and $1.69\% \text{ K}^{-1}$ for ${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$ at 313 K (Fig. S14). Subsequently, Nd^{3+} and Yb^{3+} co-doping was extended to the fluoride double perovskites Cs_2NaYF_6 (Fig. S15). Different degrees of thermal enhancement were again observed for ${}^4\text{F}_{7/2} \rightarrow {}^4\text{I}_{9/2}$, ${}^4\text{F}_{5/2} \rightarrow {}^4\text{I}_{9/2}$, and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ (Fig. S16a), with integrated intensities summarized in Fig. S16b. The LIRs (${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$), (${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$), and (${}^4\text{F}_{5/2}/{}^4\text{F}_{3/2}$) were fitted using Eq. (1), and the fits are shown in Fig. S16c–e. At 313 K, the corresponding maximum S_r values are $2.77\% \text{ K}^{-1}$ for ${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$, $1.43\% \text{ K}^{-1}$ for ${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$, and $1.37\% \text{ K}^{-1}$ for ${}^4\text{F}_{5/2}/{}^4\text{F}_{3/2}$ (Fig. S16f–h).

In LiYF_4 : 20% Yb^{3+} , 5% Nd^{3+} , various concentrations of Er^{3+} were co-doped, and 2% Er^{3+} was identified as optimal for UC luminescence under 980 nm excitation (Fig. S17). Temperature-dependent emission spectra of LiYF_4 : 20% Yb^{3+} , 5% Nd^{3+} , 2% Er^{3+} were recorded (Fig. 4c). As the temperature increased from 313 to 523 K, the integrated intensities of Er^{3+} transitions (${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) decreased to 54%, 14%, and 33% of their initial values, respectively. In contrast, the intensities of Nd^{3+} transitions (${}^4\text{F}_{7/2}$, ${}^4\text{F}_{5/2}$, and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$) increased by factors of 31.31, 4.20, and 1.41, respectively (Figs. 4d and S18). LIRs based on Nd^{3+} TCLs (${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$ and ${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$) were fitted, and the results are shown in Fig. S19. At 313 K, the maximum S_r reached 3.60% and $2.49\% \text{ K}^{-1}$, respectively, significantly improved from the original values of 1.61% and $1.69\% \text{ K}^{-1}$ (Fig. S19). This enhancement was attributed to cross-relaxation between Er^{3+} and Nd^{3+} ions (${}^4\text{F}_{9/2}(\text{Er}) + {}^4\text{I}_{9/2}(\text{Nd}) \rightarrow {}^4\text{I}_{15/2}(\text{Er}) + {}^4\text{F}_{9/2}(\text{Nd})$), which facilitated thermal coupling within the Nd^{3+} TCLs (${}^4\text{F}_{7/2}$, ${}^4\text{F}_{5/2}$, and ${}^4\text{F}_{3/2}$) (Fig. S20). Subsequently, the Nd^{3+} emission showing the strongest thermal enhancement (${}^4\text{F}_{7/2} \rightarrow {}^4\text{I}_{9/2}$) was combined with thermally quenched Er^{3+} emissions to construct Two-TCLs ratiometric thermometers. LIR values (${}^4\text{F}_{7/2}/{}^2\text{H}_{11/2}$, ${}^4\text{F}_{7/2}/{}^4\text{S}_{3/2}$, and ${}^4\text{F}_{7/2}/{}^4\text{F}_{9/2}$) were analyzed using Eq. (14) (Fig. 4e), and the corresponding fitting results are summarized in Supplementary Table S3 (The fitting results for the other LIR curves are provided in Table S4). The fitted results indicated parameter a approached zero, satisfying $b\exp(c/T) \gg a$, implying negligible influence of a on S_r . At 313 K, S_r values for $\text{LIR}({}^4\text{F}_{7/2}/{}^2\text{H}_{11/2})$, $\text{LIR}({}^4\text{F}_{7/2}/{}^4\text{S}_{3/2})$, and $\text{LIR}({}^4\text{F}_{7/2}/{}^4\text{F}_{9/2})$ reached 4.84% , 6.17% and $5.29\% \text{ K}^{-1}$, respectively (Figs. 4f and S21), outperforming most state-of-the-art luminescent thermometers (Fig. S22)^{38–41}.

To further validate the universality of this high- S_r selection strategy, the emerging fluoride double perovskites Cs_2NaYF_6 was employed as the host, co-doped

with 4% Yb^{3+} , 4% Nd^{3+} , $x\%$ Er^{3+} , and 2% Li^+ . Under 980 nm excitation, the Er^{3+} doping concentration was optimized at 2% (Fig. S23). Compared to LiYF_4 , Cs_2NaYF_6 exhibited a weaker UC quenching effect at higher Er^{3+} concentrations, attributed to its longer Y-Y interionic distances, effectively suppressing concentration quenching. Subsequently, Cs_2NaYF_6 : 4% Yb^{3+} , 4% Nd^{3+} , 2% Er^{3+} , 2% Li^+ was investigated for temperature sensing. Temperature-dependent PL spectra under 980 nm excitation are presented in Fig. S24a, and integrated intensities of Er^{3+} and Nd^{3+} transitions versus temperature are shown in Fig. S24b. As the temperature increased from 313 to 523 K, integrated intensities of Er^{3+} emissions (${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) changed to 2.53, 0.45, and 0.46 times their initial values, respectively, whereas Nd^{3+} emissions (${}^4\text{F}_{7/2}$, ${}^4\text{F}_{5/2}$, and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$) increased markedly by factors of 62.34, 6.34, and 1.38, respectively. Fitted LIRs based on Nd^{3+} TCLs (${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$, ${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$, and ${}^4\text{F}_{5/2}/{}^4\text{F}_{3/2}$) are shown in Fig. S25. Maximum S_r values at 313 K were determined as 2.82%, 1.61% and 1.34% K^{-1} , respectively, slightly higher than those of Nd^{3+} -only doped samples (2.77%, 1.43% and 1.37% K^{-1}). Furthermore, LIR fitting was conducted by combining the Nd^{3+} transition exhibiting the most significant thermal enhancement (${}^4\text{F}_{7/2} \rightarrow {}^4\text{I}_{9/2}$) and the thermally quenched Er^{3+} transitions (${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$), in accordance with Eq. (14) (Fig. S26a–c). The corresponding S_r values at 313 K were determined to be 2.74%, 4.02% and 3.85% K^{-1} , respectively (Figs. 4g and S26d–f), confirming the broad applicability of the design strategy across different host lattices.

The δT is a critical parameter for evaluating the precision of temperature readout and can be calculated using Eq. (S2) in Supplementary Note 2. In general, $\delta\text{LIR}/\text{LIR}$ is taken as 0.5%, a value corresponding to the signal-to-noise ratio of the detector⁴². The temperature-dependent δT values for LiYF_4 : 20% Yb^{3+} , 5% Nd^{3+} , 2% Er^{3+} , calculated from LIRs (${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$, ${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$) and (${}^4\text{F}_{7/2}/{}^2\text{H}_{11/2}$, ${}^4\text{F}_{7/2}/{}^4\text{S}_{3/2}$, ${}^4\text{F}_{7/2}/{}^4\text{F}_{9/2}$), are presented in Fig. S27. At 313 K, the minimum δT value for $\text{LIR}({}^4\text{F}_{7/2}/{}^4\text{F}_{3/2})$ reached only 0.08 K, and even at 523 K, it remained as low as 0.23 K. In the case of Cs_2NaYF_6 : 4% Yb^{3+} , 4% Nd^{3+} , 2% Er^{3+} , 2% Li^+ , corresponding δT values derived from LIRs (${}^4\text{F}_{5/2}/{}^4\text{F}_{3/2}$, ${}^4\text{F}_{7/2}/{}^4\text{F}_{3/2}$, ${}^4\text{F}_{7/2}/{}^4\text{F}_{5/2}$) and (${}^4\text{F}_{7/2}/{}^2\text{H}_{11/2}$, ${}^4\text{F}_{7/2}/{}^4\text{S}_{3/2}$, ${}^4\text{F}_{7/2}/{}^4\text{F}_{9/2}$) are illustrated in Fig. S28. A minimum δT of 0.12 K was observed at 313 K for $\text{LIR}({}^4\text{F}_{7/2}/{}^4\text{S}_{3/2})$, which slightly increased to 0.35 K at 523 K.

High-brightness flexible ultrathin microscale thermosensing patches

High-brightness, flexible and ultrathin LIR-based thermosensing patches are attracting considerable attention for cutting-edge applications such as real-time biomedical



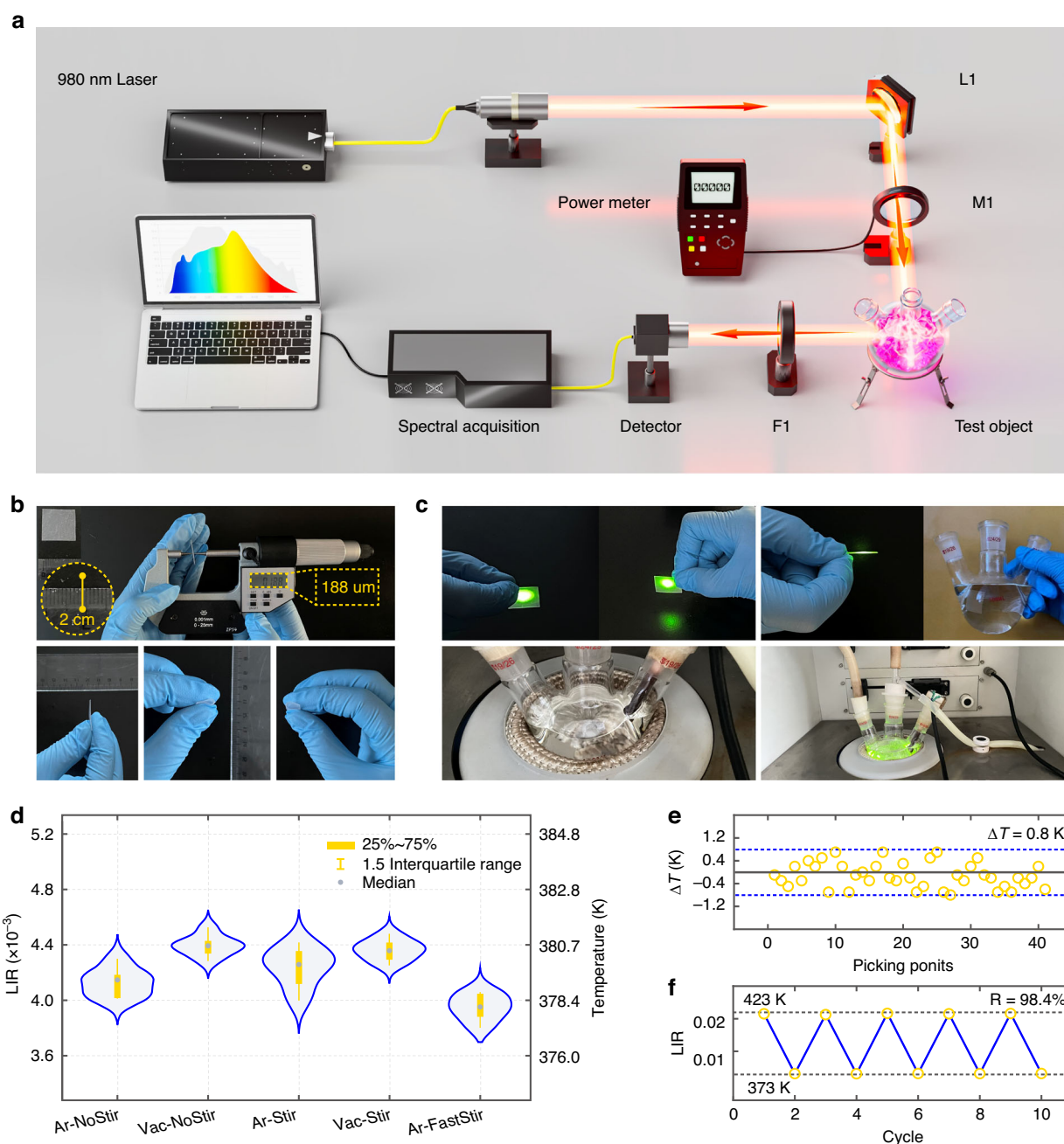


Fig. 5 High-brightness, ultrathin, and flexible thermosensing patches for in situ temperature monitoring. **a** Schematic of the real-scene monitoring under 980 nm excitation. **b** Photographs showing the lateral size, thickness, and bendability of the high-brightness flexible ultrathin microscale thermosensing patches (HFMTs), demonstrating conformal contact with both flat and curved substrates. **c** Images of the ultra-bright luminescence of the HFMT under 980 nm irradiation and demonstration of in situ temperature measurement. **d** LIR-derived temperature fluctuations under distinct operating conditions: argon flow (Ar-NoStir), vacuum (Vac-NoStir), argon flow with 20 rpm stirring (Ar-Stir), vacuum with 20 rpm stirring (Vac-Stir), and argon flow with 100 rpm stirring (Ar-FastStir). The temperature controller remained active throughout. **e** Statistical analysis of the deviations between LIR-derived and thermocouple-measured temperatures. **f** Repeatability of the LIR readout over five heating and cooling cycles between 373 and 423 K

monitoring, precise thermal management in microelectronic devices, and temperature mapping on complex curved surfaces (Fig. 5a). Thermosensitive LiYF_4 : 20% Yb^{3+} , 5% Nd^{3+} , 2% Er^{3+} phosphors were homogeneously

mixed with a prepolymer of polydimethylsiloxane (PDMS) at an optimized ratio. As illustrated in Fig. 5b, the resulting high-brightness flexible ultrathin microscale thermosensing patch (HFMT) exhibited a square shape



with a side length of 2 cm, which can be tailored to specific application requirements. The thickness, measured using an electronic micrometer with 1 μm precision, was only 188 μm . Notably, outstanding mechanical robustness was demonstrated; even after repeated bending at $\pm 180^\circ$, the structural integrity was fully retained. This microscale thinness, combined with excellent flexibility, enabled seamless adaptation to a variety of complex surfaces and dynamic environments. In LIR-based temperature sensing, emission intensity plays a critical role as it directly influences the signal-to-noise ratio. Nevertheless, achieving high-brightness UC luminescence in microscale films remains challenging due to the limited volume of active material. The fabricated HFMTTP exhibited exceptionally bright green UC emission under low-threshold 980 nm laser excitation (continuous-wave mode, $\sim 0.64 \text{ W cm}^{-2}$), as shown in Fig. 5c. Strong green luminescence was clearly visible under laser irradiation from both the front and rear sides of the patch, and pronounced lateral emission was also observed from a top view. This outstanding brightness enabled multi-angle optical signal acquisition, thereby expanding the potential application of the patch in advanced thermal sensing scenarios.

The practical applicability of the HFMTTP was validated by conducting in situ temperature monitoring, during which the patch was attached to the inner wall of a three-neck flask (Fig. 5c). In contrast to conventional thermocouples, this non-contact approach avoided direct interference with the reaction system while preserving an airtight environment, which is particularly beneficial for atmosphere-sensitive synthetic processes. Under 980 nm laser excitation, strong green UC luminescence was emitted from the HFMTTP, allowing reliable signal acquisition under complex reaction conditions. A K-type thermocouple served as the reference for monitoring the temperature of the heating solution. Simultaneously, UC spectra were collected under 980 nm excitation, and the LIR between the $\text{Nd}^{3+} {}^4\text{F}_{7/2}$ and $\text{Er}^{3+} {}^4\text{S}_{3/2}$ transitions was calculated. Using the previously established calibration curve correlating LIR with temperature, the recorded LIR values were converted into temperature readings. To emulate a typical nanoparticle synthesis environment^{43–45}, oleic acid and 1-octadecene were introduced into a three-neck flask at a 1:2 ratio. Five operating conditions were investigated: argon flow without stirring (Ar-NoStir), vacuum without stirring (Vac-NoStir), argon flow with 20 rpm stirring (Ar-Stir), vacuum with 20 rpm stirring (Vac-Stir), and argon flow with 100 rpm stirring (Ar-FastStir). For the argon-flow cases, the Ar flow rate was set to 20 mL min^{-1} . A K-type thermocouple was kept in direct contact with the thermosensing patch, and once the temperature-control unit reached a steady state, the temperature readout was recorded immediately via the

LIR signal to resolve subtle temperature fluctuations, as shown in Fig. 5d.

Moreover, precision was quantitatively evaluated based on the temperature deviation (ΔT), defined as:

$$\Delta T = T_{\text{actual}} - T_{\text{LIR}} \quad (16)$$

where T_{actual} is the temperature measured by the thermocouple, and T_{LIR} is the value derived from the LIR. Statistical analysis of 40 independent measurements revealed a maximum ΔT of only 0.8 K (Fig. 5e). Repeatability was further assessed using a reproducibility index R , defined as⁴⁶:

$$R = 1 - \frac{\text{Max}(|\text{LIR}_c - \text{LIR}_i|)}{\text{LIR}_c} \quad (17)$$

in which LIR_c represents the standard value from the calibration curve, and LIR_i denotes the corresponding value for each measurement. An R value of 98.4% was obtained, confirming excellent measurement repeatability (Fig. 5f). These findings collectively demonstrate that the HFMTTP possesses high resolution ($< 0.8 \text{ K}$), fast response, and strong reproducibility, highlighting its potential to replace traditional contact-based sensors and infrared thermography in biomedical and microelectronic thermal management applications.

Discussion

In conclusion, we establish a population-dynamics framework that quantitatively defines the onset temperature and thermal coupling window for Boltzmann-type luminescent nanothermometry. A key insight from this model is the derivation of a practical criterion ($\Delta E_{\text{lower}} \gtrsim 2\Delta E$) for stable thermal coupling, which rationalizes how adjacent energy levels disrupt population equilibrium and provides a clear guideline for selecting suitable energy level pairs. Beyond defining the conditions for valid coupling, we introduced a splitting factor to bridge macroscopic sensitivity with microscopic chemical bonding, enabling predictive design beyond empirical trial-and-error. In addition, a dual-emitter scheme combining thermally quenched Er^{3+} and thermally enhanced Nd^{3+} channels achieves record sensitivities of $6.17\% \text{ K}^{-1}$ with sub-0.1 K resolution, while high-brightness, flexible, ultrathin PDMS patches demonstrate $< 0.8 \text{ K}$ deviation and 98.4% reproducibility in situ. Together, these insights and demonstrations provide mechanistic principles and practical guidelines for the rational development of next-generation high-precision luminescent nanothermometers.



Materials and methods

Chemicals

LiF ($\geq 99\%$, Beijing Chemical Factory); NaF ($\geq 99\%$, Beijing Chemical Factory); LiNO_3 ($\geq 99\%$, Beijing Chemical Factory); NH_4F ($\geq 96\%$, Titan Scientific); $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aladdin); $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aladdin); $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aladdin); $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aladdin); $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Aladdin); Y_2O_3 ($\geq 99.99\%$, Aladdin); Yb_2O_3 ($\geq 99.99\%$, Aladdin); Er_2O_3 ($\geq 99.99\%$, Aladdin); Nd_2O_3 ($\geq 99.99\%$, Aladdin); Cs_2CO_3 ($\geq 99.9\%$, Macklin); Na_2CO_3 ($\geq 99\%$, Beijing Chemical Factory); Li_2CO_3 ($\geq 99\%$, Shanghai Reagent Second Factory). All chemicals were used as received without further purification (purities per supplier specifications).

Synthesis

Synthesis of $\text{LiYF}_4: x\text{Ln}^{3+}$ ($\text{Ln} = \text{Er}, \text{Yb}, \text{Nd}$) phosphors: a typical preparation used $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) and LiF (4 mmol) in the desired molar ratio. The solids were placed in a beaker and wetted dropwise with deionized water (10 mL) under stirring for 30 min to afford a clear solution. In a second beaker, NH_4F (32 mmol) was dissolved in deionized water (20 mL) and stirred for 30 min. The Ln/Li solution was added slowly to the NH_4F solution and the mixture stirred for a further 30 min, then transferred to a Teflon-lined stainless-steel autoclave and heated at 200°C for 24 h. The resulting microcrystals were collected by centrifugation, washed with deionized water and ethanol, and dried at 60°C for 24 h.

Synthesis of $\text{Cs}_2\text{NaYF}_6: x\text{Ln}^{3+}, y\text{Li}^+$ ($\text{Ln} = \text{Er}, \text{Yb}, \text{Nd}$) phosphors: certain amounts of Cs_2CO_3 , Na_2CO_3 , Y_2O_3 , Ln_2O_3 , Li_2CO_3 , and NH_4F were weighed, combined, and ground unidirectionally in an agate mortar for 30 min to ensure homogeneity. The dried mixture was placed in a crucible and calcined in air at 700°C for 6 h, and then it was allowed to cool naturally to room temperature.

The synthesized phosphors were incorporated into a flexible PDMS matrix: the PDMS base and curing agent were thoroughly mixed at a mass ratio of 10:1, after which the phosphors were dispersed into the PDMS prepolymer under vigorous stirring to obtain a homogeneous slurry. Following vacuum degassing, the mixture was cast into custom-made silicone molds and cured at 80°C for 2 h. The cured films were then demolded to yield HFMTs, which were subsequently used for the variable-temperature luminescence measurements.

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Author contributions

Kejie Li designed and performed the experiments, analysed the data, and prepared the figures and manuscript. Jiaqi Zhao, Dongxu Guo and Ruiying Lu assisted with sample characterization and data processing. Mochen Jia guided the project and revised the manuscript. Zhiying Wang supervised the experimental methodology and data interpretation. Zuoling Fu oversaw the overall research design, coordinated the project, and finalized the manuscript. All authors discussed the results and approved the final manuscript.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflict of interest

The authors declare no competing interests.

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