

Upconversion Luminescence in $\text{Er}^{3+}/\text{Yb}^{3+}$ Co-Doped Calcium Aluminate for Optical Thermometry

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Abstract: Luminescence thermometry offers remote, fast and minimally invasive temperature measurement. Among its probes, $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped upconversion (UC) phosphors excited near 980 nm are the most widely studied. Their two green emission bands, from the thermally coupled $^2\text{H}_{11/2}/^2\text{H}_{5/2}$ and $^4\text{S}_{3/2}/^4\text{S}_{1/2}$ levels of Er^{3+} , have an intensity ratio that follows Boltzmann statistics. Calcium aluminates (CaAl_2O_3 , $\text{CaAl}_2\text{SiO}_6$, $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{Ca}_{1-x}\text{Al}_x\text{Si}_{2-x}\text{O}_{8-x}$) are attractive host lattices because they are chemically and thermally robust, cheap to make, and have moderate phonon energies and a wide band gap. This review covers four topics. First, the structure and vibrational properties of the main calcium aluminate phases and how they accommodate lanthanide dopants. Second, the energy-transfer physics of the $\text{Er}^{3+}/\text{Yb}^{3+}$ pair. Third, the fluorescence intensity ratio (FIR) method, including its sensitivity limits, temperature uncertainty and range of validity. Fourth, the artefacts that most often compromise reported results, especially laser-induced heating and spectral overlap. The theoretical limits on relative sensitivity are quantified and a recommended reporting standard is proposed. We conclude that calcium aluminate hosts are best suited to medium- and high-temperature sensing, and that a systematic same-conditions comparison across the aluminate phases is the main gap in the literature..

Keywords: upconversion; $\text{Er}^{3+}/\text{Yb}^{3+}$; calcium aluminate; fluorescence intensity ratio; optical thermometry; thermally coupled levels; luminescence thermometry

I. INTRODUCTION

Temperature is one of the most frequently measured physical quantities, yet conventional contact sensors such as thermocouples and resistance thermometers have limits. They are difficult to use in electromagnetically noisy environments, on moving or rotating parts, in corrosive media, in microscopic or biological systems, and on surfaces that cannot be touched without disturbing them. Luminescence thermometry avoids these limits by reading temperature from an optical signal. The signal may be emission intensity, band ratio, band position, bandwidth or excited-state lifetime of a probe material [1–3].

Trivalent lanthanide ions are particularly useful probes. Their 4f electrons are shielded by filled 5s and 5p shells, so their emission bands are narrow and only weakly perturbed by the host. Many 4f levels are metastable and long-lived. The ladder-like level structure also allows upconversion, the conversion of two or more low-energy photons into one higher-energy photon [4,5]. UC thermometry has two practical advantages. Near-infrared excitation penetrates many media well, and anti-Stokes emission largely avoids autofluorescence and scattered excitation light.

The $\text{Er}^{3+}/\text{Yb}^{3+}$ pair is the most studied UC couple. Yb^{3+} absorbs strongly near 980 nm ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) and transfers its energy efficiently to Er^{3+} . Er^{3+} has two closely spaced excited levels, $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$, separated by roughly 700–800 cm^{-1} . Their populations are therefore in thermal contact over a wide temperature range. This is the basis of the FIR technique reviewed by Wade et al. [6].



The host lattice determines the local crystal field, the dopant site symmetry, the maximum phonon energy (and hence the non-radiative rates), the thermal stability and the achievable doping level. Fluorides such as NaYF_4 give very high UC efficiency because of their low phonon energies (about 350 cm^{-1}), but they are less robust chemically and thermally. Oxides are more stable but have higher phonon energies. Calcium aluminates are a useful compromise. They are refractory, inexpensive and well characterised, and they have moderate phonon energies. This review explains why they are promising hosts for UC thermometry and how such thermometers should be evaluated.

The article is organised as follows. Section 2 describes the host lattices. Section 3 covers the spectroscopy and upconversion mechanisms of $\text{Er}^{3+}/\text{Yb}^{3+}$. Section 4 develops the theory of FIR thermometry. Section 5 treats experimental artefacts. Section 6 discusses the host-specific considerations. Section 7 proposes a reporting standard. Section 8 outlines perspectives and applications.

II. CALCIUM ALUMINATE HOST LATTICES

2.1 Phases in the $\text{CaO-Al}_2\text{O}_3$ system

The $\text{CaO-Al}_2\text{O}_3$ system contains several stable compounds. Those relevant as luminescent hosts are summarised in Table 1.

Table 1. Principal calcium aluminate phases.

Phase	Common name	Crystal system	Space group	Key structural feature
CaAl_2O_4 (CA)	Krotite	Monoclinic	$\text{P2}_1/\text{n}$	Corner-sharing AlO_4 tetrahedra forming tunnels; three distinct Ca sites
CaAl_4O_7 (CA_2)	Grossite	Monoclinic	$\text{C2}/\text{c}$	AlO_4 tetrahedral framework
$\text{CaAl}_{12}\text{O}_{19}$ (CA_6)	Hibonite	Hexagonal	$\text{P6}_3/\text{mmc}$	Magnetoplumbite-type; Al in several coordinations
$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C12A7)	Mayenite	Cubic	I-43d	Cage framework with extra-framework oxygen species

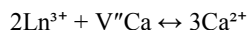
In CaAl_2O_4 the aluminate framework is built entirely of AlO_4 tetrahedra. The large tunnels host the Ca^{2+} ions, which occupy three crystallographically distinct sites [12]. Mayenite is notable because its positively charged cage framework can encapsulate anions such as O^{2-} , OH^- or even electrons. This led to extensive work by Hosono and co-workers on the conversion of this insulating oxide into a conductor [13,14]. For lanthanide luminescence, the key points are that the phase obtained depends on the stoichiometry, precursor reactivity and thermal history, and that each phase offers different Ca^{2+} environments for the dopant.

2.2 Dopant substitution and charge compensation

Trivalent lanthanide dopants are expected to substitute Ca^{2+} , the only cation of comparable size. Shannon's ionic radii in six-fold coordination are approximately $1.00 \text{ \AA}$ for Ca^{2+} , $0.89 \text{ \AA}$ for Er^{3+} , $0.868 \text{ \AA}$ for Yb^{3+} and $0.535 \text{ \AA}$ for Al^{3+} ($0.39 \text{ \AA}$ in four-fold coordination) [7]. Both lanthanide ions are far too large for the tetrahedral Al^{3+} sites, so Ca^{2+} is the natural substitution site.

Replacing Ca^{2+} with Ln^{3+} creates a positive charge excess that must be compensated. The common mechanisms are: calcium vacancies, $2\text{Ln}^{3+} + \text{V}''\text{Ca} \leftrightarrow 3\text{Ca}^{2+}$ (written in full below); interstitial oxygen; co-doping with a monovalent ion (Li^+ , Na^+ , K^+) on a Ca^{2+} site; partial substitution of Al^{3+} by a lower-valent species, which is less common.





The compensation mechanism changes the local symmetry around the lanthanide ion, and with it the electric-dipole transition probabilities and the relative intensity of the emission bands. Alkali-ion co-doping is also widely reported to modify UC intensity in oxide hosts, usually by reducing local symmetry and suppressing defect-related quenching. Any comparison between studies must therefore take the compensation route into account.

2.3 Phonon energy and non-radiative relaxation

The multiphonon relaxation rate between two levels separated by an energy gap ΔE falls approximately exponentially with the number of phonons p needed to bridge the gap, a relation established in the classic work on rare-earth non-radiative decay [15]:

$$p = \frac{\Delta E}{\hbar \omega_{\max}} \quad (1)$$

where $\hbar \omega_{\max}$ is the maximum phonon energy of the host. Lower $\hbar \omega_{\max}$ means weaker quenching of intermediate levels such as $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ of Er^{3+} , and so higher UC efficiency.

Calcium aluminates have higher maximum phonon energies than fluorides (NaYF_4 is about 350 cm^{-1}) but lower than borates or phosphates, whose maxima lie above 1000 cm^{-1} . For the aluminate phases the highest-energy vibrations are the AlO_4 stretching modes, typically reported in the range of roughly $700\text{--}900 \text{ cm}^{-1}$, with the exact value depending on the phase. This has two consequences:

Overall UC quantum yield is expected to be lower than in the best fluoride hosts.

Non-radiative bridging of the $\sim 700\text{--}800 \text{ cm}^{-1}$ gap between $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ takes only one phonon, which assures fast thermal equilibration between the two levels. This is helpful for the Boltzmann assumption.

The second point is often overlooked. A host with phonon energy comparable to or higher than the $^2\text{H}_{11/2}\text{--}^4\text{S}_{3/2}$ gap guarantees efficient thermalisation of the two levels, which supports the validity of the FIR method.

III. SPECTROSCOPY OF THE $\text{Er}^{3+}/\text{Yb}^{3+}$ PAIR

3.1 Electronic structure and transition intensities

Er^{3+} has the configuration $[\text{Xe}]4f^1$. The relevant multiplets, in order of increasing energy, are $^4\text{I}_{15/2}$ (ground), $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{9/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$ and $^4\text{F}_{7/2}$. Intraconfigurational $4f\text{--}4f$ transitions are parity-forbidden for the free ion. In a solid they gain intensity because odd-parity crystal-field components mix opposite-parity configurations into the $4f$ states. Judd–Ofelt theory, published independently by Judd and Ofelt in 1962 [8,9], describes this with three phenomenological parameters, Ω_2 , Ω_4 and Ω_6 .

The $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition is a hypersensitive transition: its intensity depends strongly on the local environment through Ω_2 . Because the thermometric signal is the ratio of this band to the $^4\text{S}_{3/2}$ band, the host-dependent pre-exponential factor of the FIR expression (Section 4.2) varies from one host to another.

Yb^{3+} ($[\text{Xe}]4f^{13}$) has only two multiplets, $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$, separated by about $10,000 \text{ cm}^{-1}$. This simple structure avoids excited-state absorption and parasitic cross-relaxation within Yb^{3+} itself, which is why it is an excellent sensitizer.

3.2 Upconversion mechanisms

Under 980 nm excitation the main processes are [4,5,16]:

Ground-state absorption (GSA). Yb^{3+} ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) absorbs a photon. Er^{3+} can also absorb directly ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$), but with a much smaller cross-section.

Energy transfer upconversion (ETU).

Step 1: $\text{Yb}^{3+}(^2\text{F}_{5/2}) + \text{Er}^{3+}(^4\text{I}_{15/2}) \rightarrow \text{Yb}^{3+}(^2\text{F}_{7/2}) + \text{Er}^{3+}(^4\text{I}_{11/2})$

Step 2: $\text{Yb}^{3+}(^2\text{F}_{5/2}) + \text{Er}^{3+}(^4\text{I}_{11/2}) \rightarrow \text{Yb}^{3+}(^2\text{F}_{7/2}) + \text{Er}^{3+}(^4\text{F}_{7/2})$



Non-radiative relaxation of ${}^4F_{7/2}$ to ${}^2H_{11/2}$ and ${}^4S_{3/2}$, followed by green emission:

${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ (about 520–530 nm)

${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ (about 540–560 nm)

Red emission (${}^4F_{9/2} \rightarrow {}^4I_{15/2}$, about 650–670 nm) is fed by multiphonon relaxation from ${}^4S_{3/2}$ and by a second route, in which ${}^4I_{11/2}$ relaxes to ${}^4I_{13/2}$ and a further transfer from Yb^{3+} raises it to ${}^4F_{9/2}$. Cross-relaxation (for example ${}^2H_{11/2} + {}^4I_{15/2} \rightarrow {}^4I_{9/2} + {}^4I_{13/2}$) also contributes at high Er^{3+} concentrations.

Because a host with relatively high phonon energy accelerates the relaxation of ${}^4I_{11/2}$ and of the green levels, red emission is often comparatively strong in oxide hosts. This is a general trend, not a rule.

3.3 Power dependence

In the unsaturated regime, an n-photon UC process gives

$$I_{UC} \propto P^n \quad (2)$$

where P is the pump power. For the Er^{3+} green bands n is expected to approach 2. Pollnau et al. showed that when upconversion competes with linear decay for depopulation of the intermediate level, the slope falls below the ideal value and tends toward 1 at high power [17]. Measured slopes therefore carry mechanistic information, and a slope that changes with power marks the onset of saturation. The same power range is also where laser-induced heating becomes a concern (Section 5.1).

3.4 Concentration effects

Yb^{3+} is the sensitizer and is normally used at much higher concentration than Er^{3+} , from a few mol% to a few tens of mol%. Er^{3+} is typically kept at about 0.5–2 mol% to limit cross-relaxation and energy migration to quenching sites. These are customary ranges only. The optimum for a given host balances absorption (more Yb^{3+} is better), back-transfer from Er^{3+} to Yb^{3+} , and concentration quenching, so it must be determined experimentally. In FIR thermometry a further consideration applies. Concentration changes alter the red-to-green ratio but should not alter the ratio of the two green bands, which is one reason the thermally coupled pair is preferred over other band pairs.

IV. THEORY OF FIR THERMOMETRY

4.1 Thermally coupled levels

Two excited levels are thermally coupled when ΔE is small enough that thermal energy can populate the upper level from the lower one, and large enough that the two emission bands can be resolved. Wade et al. gave a practical range of roughly 200 to 2000 cm^{-1} [6]. For Er^{3+} the ${}^2H_{11/2}$ – ${}^4S_{3/2}$ gap is typically around 700–800 cm^{-1} , with modest variation among hosts.

Under quasi-thermal equilibrium the populations follow the Boltzmann distribution:

$$\frac{N_H}{N_S} = \frac{g_H}{g_S} \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (3)$$

where H and S denote ${}^2H_{11/2}$ and ${}^4S_{3/2}$, $g = 2J + 1$ are the degeneracies, $k_B = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$ is the Boltzmann constant and T is the absolute temperature.

4.2 The FIR expression

The fluorescence intensity ratio of the two bands is

$$R = \frac{I_H}{I_S} = B \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (4)$$

with I_H and I_S the integrated intensities of the ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ emissions. The pre-exponential factor is



$$B = \frac{g_H A_H h \nu_H}{g_S A_S h \nu_S} \quad (5)$$

where A are the spontaneous emission rates, h is Planck's constant and ν the emission frequencies. Since the A values depend on the host through the Judd–Ofelt parameters, B is a host-dependent fitted quantity, not a universal constant. A common extended form,

$$R = B \exp\left(-\frac{\Delta E}{k_B T}\right) + C \quad (6)$$

includes an offset C to absorb spectral overlap. It should be used only with justification, because a free offset can improve a fit without improving the physics.

Because R is a ratio of two intensities from the same emitter, it is largely independent of excitation fluctuations, probe concentration and detector gain. This self-referencing is the main advantage over single-band intensity thermometry.

4.3 Sensitivity

Two sensitivity definitions are in standard use [3,10]:

Absolute sensitivity:

$$S_a = \left| \frac{dR}{dT} \right| = R \cdot \frac{\Delta E}{k_B T^2} \quad (7)$$

Relative sensitivity:

$$S_r = \frac{1}{R} \left| \frac{dR}{dT} \right| = \frac{\Delta E}{k_B T^2} \quad (8)$$

S_r , expressed in % K⁻¹, is the correct figure of merit for comparing thermometers, because it does not depend on the absolute value of R or on the instrument. Two properties follow directly from Equation (8). S_r grows linearly with ΔE and falls as 1/T². Table 2 gives values calculated from the formula for two representative energy gaps.

Table 2. Relative sensitivity S_r (% K⁻¹) calculated from $S_r = \Delta E/(k_B T^2)$.

T (K)	$\Delta E = 700 \text{ cm}^{-1}$	$\Delta E = 800 \text{ cm}^{-1}$
300	1.12	1.28
400	0.63	0.72
500	0.40	0.46
600	0.28	0.32
800	0.16	0.18
1000	0.10	0.12

The table shows the physical ceiling of the Er³⁺ green-band thermometer. A relative sensitivity of about 1 % K⁻¹ is reachable only near room temperature, and it drops by an order of magnitude by 1000 K. Reports of S_r far above these values for the thermally coupled pair deserve scrutiny, since they may reflect spectral overlap errors or non-thermal effects. Larger apparent sensitivities are possible with non-thermally-coupled pairs, but these depend on pump power and dopant concentration and are less reliable [3].

4.4 Temperature uncertainty and resolution

Sensitivity does not by itself determine performance. The temperature uncertainty is



$$\delta T = \frac{1}{S_r} \frac{\delta R}{R} \quad (9)$$

where $\delta R/R$ is the relative uncertainty of the measured ratio, set by detector noise and the signal-to-noise ratio of the weaker band. As an illustration, for $\delta R/R = 1\%$ and $S_r = 1.1\% \text{ K}^{-1}$ (300 K), $\delta T \approx 0.9 \text{ K}$. For the same $\delta R/R$ at $S_r = 0.28\% \text{ K}^{-1}$ (600 K, $\Delta E = 700 \text{ cm}^{-1}$), $\delta T \approx 3.6 \text{ K}$. Uncertainty thus rises quickly at high temperature unless signal quality improves, which is why the signal-to-noise ratio of the weak band, the integration time and the detector must be reported.

Repeatability is commonly defined as

$$R_p = 1 - \frac{\max|\Delta_c - \Delta_i|}{\Delta_c} \quad (10)$$

where Δ_c is the mean value of the thermometric parameter at a given temperature over repeated cycles and Δ_i is an individual measurement [3].

4.5 Validity limits of the Boltzmann model

The Boltzmann model assumes that the two levels are in thermal equilibrium. It fails in these situations:

when the rates of depopulation of the levels are comparable to the thermalisation rate between them;

when strong concentration quenching or energy migration populates the levels non-thermally;

when the two bands overlap and are not separated properly;

at the low-temperature end, where the upper level is so weakly populated that its band is lost in noise;

at the high-temperature end, where thermal quenching removes signal from both levels.

Suta and Meijerink provided a thermodynamic and kinetic framework for the operating range of ratiometric single-ion thermometers [11]. A practical consistency check follows from it. The ΔE obtained from fitting $\ln R$ against $1/T$ should be close to the spectroscopic energy gap measured between the band centres. A large discrepancy points to overlap or non-thermal effects.

V. EXPERIMENTAL ARTEFACTS AND GOOD PRACTICE

5.1 Laser-induced heating

Laser-induced heating is among the most common sources of error in UC thermometry. Under 980 nm excitation the phosphor dissipates part of the absorbed energy non-radiatively, and many matrices and any residual water absorb as well. The sample temperature can thus exceed the nominal stage or ambient temperature, and the apparent calibration becomes a function of pump power. For a host with low UC efficiency, the high power density needed to obtain a usable signal makes the problem worse. Good practice includes:

using the lowest power density that gives adequate signal-to-noise, reported in W cm^{-2} ;

verifying that FIR is independent of pump power at fixed stage temperature;

using modulated or pulsed excitation where possible;

keeping the beam spot size and geometry identical for calibration and measurement;

treating any systematic dependence of FIR on power as a heating signal, and not presenting the sample as an unperturbed thermometer in that regime.

5.2 Spectral treatment

The two green bands overlap partly, and the overlap increases at elevated temperature as the $^2\text{H}_{11/2}$ band broadens. Fixed-window integration (the same windows at all temperatures) and Gaussian or Lorentzian deconvolution are both used. The choice must be stated and applied consistently, since it directly affects R and therefore ΔE and S_r . Background subtraction and correction for the spectral response of the detection system are essential. Reabsorption in



thick, concentrated powders can also distort the ratio, because the $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission can be reabsorbed by ground-state Er^{3+} .

5.3 Calibration and temperature control

An independent, calibrated temperature sensor should be placed as close to the sample as possible. Sufficient equilibration time must be allowed at each set point, and heating-cooling cycles should be performed to reveal hysteresis. A thermometer that has been calibrated only on heating cannot be assumed to be reversible.

5.4 Thermal quenching

Both green emissions decay at high temperature through multiphonon and other non-radiative processes. Thermal quenching limits the usable upper temperature and sets the signal-to-noise ceiling there. The refractory character of calcium aluminates helps by keeping the host structurally stable at temperatures where many other hosts decompose, but it does not remove intrinsic quenching of the Er^{3+} levels.

VI. Er^{3+}/Yb^{3+} IN CALCIUM ALUMINATE HOSTS

6.1 Synthesis routes

Several routes are used to prepare calcium aluminate phosphors:

Solid-state reaction: mixing $CaCO_3$ (or CaO), Al_2O_3 , Er_2O_3 and Yb_2O_3 , with repeated grinding and calcination above about 1200 °C. It is simple and scalable but tends to give coarse particles and a less uniform dopant distribution.

Combustion synthesis: a self-sustaining reaction between metal nitrates and an organic fuel such as urea or glycine, giving fine, porous powders quickly. Residual carbon and rapid cooling can leave defects, so post-annealing is common.

Sol-gel and Pechini (citrate) methods: better mixing at the molecular level and lower crystallisation temperatures, with finer control of composition.

Because phase formation in the $CaO-Al_2O_3$ system is sensitive to the Ca/Al ratio and thermal history, mixed-phase products are common. Since each phase offers different Ca^{2+} sites and phonon spectra, thermometric properties reported for one phase cannot be transferred to another, and phase purity should be established by X-ray diffraction.

6.2 Structural implications for thermometry

In $CaAl_2O_4$ the three Ca^{2+} sites are inequivalent. Er^{3+} ions distributed over several sites with different crystal fields give inhomogeneously broadened emission bands, which complicates the separation of the two green bands but does not alter the Boltzmann physics so long as the sites are in mutual thermal equilibrium. In C12A7 the cage framework and extra-framework oxygen species provide additional charge-compensation routes and defect chemistry. $CaAl_4O_7$ and $CaAl_{12}O_{19}$ offer other Ca^{2+} environments, with $CaAl_{12}O_{19}$ being especially stable at high temperature. A systematic comparison of the four phases, prepared by the same route and measured under identical conditions, would be the most informative step toward selecting the best host. To our knowledge such a head-to-head comparison remains scarce.

6.3 Advantages

Three advantages are widely recognised for aluminate hosts.

First, **thermal and chemical stability**. Calcium aluminates are refractory materials used in cements and ceramics, so they tolerate conditions that would degrade polymer or fluoride hosts. Since S_r of any Er^{3+} FIR thermometer decreases as $1/T^2$, a stable host does not raise sensitivity at high temperature but does extend the usable range upward, which is where non-contact optical methods are most valuable.

Second, **moderate phonon energy and a wide band gap**. Aluminate phonon energies are higher than those of fluorides but lower than those of borates and phosphates. The wide band gap avoids host absorption of the green emission and of the 980 nm excitation.



Third, **low cost and simple synthesis**. The raw materials are abundant, and well-characterised preparation routes exist.

6.4 Limitations

The relative sensitivity of the $^2H_{11/2}/^4S_{3/2}$ pair is bounded by the energy gap and falls as $1/T^2$, regardless of host. The higher phonon energy lowers UC quantum yield relative to fluorides, which in turn forces higher excitation power and increases the risk of laser heating. The multi-site nature of Ca^{2+} leads to inhomogeneous broadening and overlap of the green bands. Finally, dopant incorporation depends on charge compensation, which makes reproducibility between laboratories more difficult unless the compensation strategy is controlled.

6.5 Strategies for improvement

Several approaches reported for Er^{3+} thermometry in general could be applied to aluminates.

Alternative thermometric parameters. Using non-thermally-coupled pairs (green and red bands, or different ions) can raise apparent sensitivity, but the ratio then depends on dopant concentration and pump power and needs careful treatment [3].

Multi-parameter readout. Combining FIR with lifetime-based readout provides a more robust thermometer and a cross-check against artefacts [2].

Alternative sensitisers and co-dopants. Using Tm^{3+} , Nd^{3+} or other ions as extra thermometric channels in the same host increases the information obtained.

Particle engineering. Core-shell architectures reduce surface quenching, but they matter mainly for nanocrystals and less for bulk ceramic powders [5].

Alkali co-doping. This tunes local symmetry and defect concentration, and can raise UC efficiency, which allows lower pump power.

VII. RECOMMENDED REPORTING STANDARD

Comparison between studies is hampered by inconsistent reporting. We recommend that future work on Er^{3+}/Yb^{3+} calcium aluminate thermometers report at least the items in Table 3.

Table 3. Recommended minimum reporting for UC thermometry studies.

Category	Items to report
Material	Phase (by XRD), dopant concentrations (mol%), charge-compensation method, synthesis route and annealing conditions
Vibrational properties	Maximum phonon energy from Raman or FTIR
Excitation	Wavelength, CW or pulsed, power density ($W\ cm^{-2}$), spot size
Power dependence	Log-log slope for each band; evidence that FIR is power-independent in the working range
Spectral analysis	Integration windows or deconvolution method; spectral-response correction
Calibration	Temperature range, sensor placement, equilibration time, heating and cooling cycles
Fit results	Fitted ΔE compared with the spectroscopic gap; B (and C if used); fit quality
Performance	S_a and S_r as functions of T; temperature uncertainty δT with measurement conditions; repeatability
Comparison	Values for the same host measured under the same conditions where possible



Reporting S_r at its maximum only, without the temperature at which it occurs and without δT , gives an incomplete picture. A good thermometer is one whose uncertainty is acceptable over the whole stated range, not one with a single impressive sensitivity value.

VIII. PERSPECTIVES AND APPLICATIONS

8.1 Application areas

Because calcium aluminates are refractory and Er^{3+} FIR thermometers are most useful where contact sensors fail, the most plausible applications are in medium- and high-temperature settings. Examples include non-contact monitoring of heated components, diagnostics of thermal-barrier-type ceramic coatings, temperature sensing in furnaces and combustion-related environments, and luminescent sensor layers on ceramic substrates. For microscale or biological sensing, nanoscale fluoride hosts remain more efficient, and aluminate nanoparticles would need to demonstrate competitive brightness. The suitability of any phosphor for a given application depends on the sensitivity, uncertainty and stability actually demonstrated, not on the host's general properties.

8.2 Open research questions

Systematic phase comparison. Which aluminate phase gives the best compromise between UC efficiency, thermal stability and spectral separation of the green bands under identical conditions?

Charge compensation. How do different compensators (Li^+ , Na^+ , K^+ , vacancies) change site symmetry, B, and brightness?

High-temperature limits. What is the true upper operating temperature, taking thermal quenching and signal-to-noise into account?

Heating-aware calibration. Can pump-power-dependent heating be modelled and corrected, so that low-efficiency oxides can be used reliably?

Multi-parameter approaches. Does combining FIR with lifetime or with a second ion improve accuracy beyond the intrinsic $1/T^2$ limit of S_r ?

Long-term stability. How does repeated thermal cycling affect the phase, defect structure and calibration?

IX. CONCLUSIONS

The $\text{Er}^{3+}/\text{Yb}^{3+}$ pair in a calcium aluminate host combines efficient 980 nm sensitisation with a Boltzmann-coupled green doublet, which gives a self-referenced FIR thermometric signal. Its fundamental properties are set by two quantities. The energy gap ΔE between the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels fixes the relative sensitivity through $S_r = \Delta E/(k_B T^2)$, giving values of about 1 % K^{-1} near room temperature and falling to about 0.1 % K^{-1} near 1000 K. The host phonon spectrum fixes the balance between radiative and non-radiative decay. Calcium aluminates are promising hosts because of their refractory character, moderate phonon energies, wide band gap and low cost. These properties favour medium- and high-temperature sensing more than room-temperature or biological use. Their main drawbacks are lower UC efficiency than fluorides, inhomogeneous broadening from multiple Ca^{2+} sites, and a greater risk of laser-induced heating. Reliable results require phase-verified samples, stated doping and charge compensation, consistent spectral analysis, controlled excitation power, and reporting of sensitivity together with temperature uncertainty and repeatability. A systematic, same-conditions comparison of the aluminate phases is the most valuable next step for the field.

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