Sensors for optical thermometry based on luminescence from layered $\text{YVO}_4$: Ln$^{3+}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) thin films made by atomic layer deposition

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Below the Earth’s crust, temperatures may reach beyond 600 K, impeding the batteries used to power conventional thermometers. Fluorescence intensity ratio based temperature probes can be used with optical fibers that can withstand these conditions. However, the probes tend to exhibit narrow operating ranges and poor sensitivity above 400 K. In this study, we have investigated single and dual layered $\text{YVO}_4$: Ln$^{3+}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) thin films (100–150 nm) for use in fluorescence intensity ratio based temperature sensors in the 300–850 K range. The type of lanthanide emission can be fine-tuned by adjusting the thickness of each layer, and the layered structure allows for emission from otherwise incompatible lanthanide pairs. This novel multi-layered approach enables high sensitivity over a broad temperature range. The highest relative sensitivity was achieved for a dual layered $\text{YVO}_4$: Eu$^{3+}$/YVO$_4$: Dy$^{3+}$ sample, exhibiting a maximum sensitivity of 3.6% K$^{-1}$ at 640 K. The films were successfully deposited on all tested substrates (silicon, iron, aluminum, glass, quartz, and steel), and can be applied homogenously to most surfaces without the use of binders. The films are unaffected by water, enabling non-contact temperature sensing in water, where IR thermometers are not an option.

Luminescent temperature sensors are gaining attention as remote real-time temperature sensors due to their fast response, high spatial resolution and sensitivity, and low perturbation of the sample temperature during measurements. This enables them to be used for monitoring of moving parts, such as a working engine and in vivo temperature sensing of living organisms at the micro- and nanoscale. As the signal from a luminescent probe is optical, it can pass through robust silica fibers, making them attractive for use in harsh conditions where the combination of electrical wiring and batteries is not a realistic option, e.g. in boreholes where temperatures can reach above 600 K. The advantages of luminescent temperature sensors over other non-contact temperature sensors, such as IR-thermometers, are mainly their fast response, high spatial resolution and sensitivity, self-referencing, and that they do not rely on the emissivity of the material where the temperature is to be measured, as previously reviewed.

Optical thermometry using luminescent materials can either be performed by measuring the changes in the lifetime of the excited state of the phosphor, or by measuring the difference in fluorescence intensity ratio (FIR) between two excited states that can either be thermally coupled (TCS) or non-thermally coupled (NTCS). Measurements based on the lifetime of temperature sensitive excited states requires sophisticated read-out, time-consuming data fitting, and becomes less reliable if the lifetimes are not single-exponential. FIR measurements can be performed with simple read-out at significantly reduced cost. This signal is also intrinsically referenced, as variations in emission intensity, indicator concentration, geometry, source intensity, and light field are cancelled out when the relative emission of two different states is considered. Probes based on the FIR methodology tend to either exhibit a high temperature sensitivity over a narrow operating range or poor sensitivity over a broad range.
Sm, Eu, Dy, Ho, Er, Tm, Yb, thd Y(thd)₃, VO(thd)₂ and O₃ were used as the yttrium, vanadium and oxygen precursor, respectively. All information energies, high transparency in the visible range, non-hygroscopicity, and a low symmetry Y ₃ reported on the growth of most of the lanthanide oxides from Ln(thd)₃ substituting some of the Y(thd)₃ pulses with other Ln(thd)₃ pulses.

Microchemistry Ltd) at 300 °C at a reactor pressure of ~3.6 mbar. The thin films investigated in this study were deposited with an F-120 research-type ALD-reactor (ASM Methods)

Figure 1. Concept of a thin-film material used for temperature detection over a wide temperature range. In this hypothetical material R₁₂ is the FIR from a transition in layer 1 and layer 2, which is sensitive in the 200–350 K region, while R₁₃ and R₂₃ are sensitive in the 300–500 K and 400–800 K, respectively, thus yielding a highly sensitive temperature probe over the entire 200–800 K range.

a broad range due to how these parameters are linked. As luminescence eventually quenches with temperature, most materials do not exhibit sufficient emission intensity to be useful above 500 K, severely limiting the usefulness of FIR based probes for high-temperature applications. In this study, we demonstrate how it is possible to achieve high sensitivity over large operating ranges by employing multilayered thin films produced by the atomic layer deposition (ALD) technique.

A layered thin film can contain different luminescent ions in separate layers, resulting in numerous intensity ratios, each with an independent temperature sensitivity, similar to how e.g. YAG: Cr³⁺, Nd³⁺ exhibits three different kinds of FIRs in the same material¹. By selecting luminescent ions whose emission quenches in different temperature ranges, it is possible to achieve high temperature sensitivity over a broad temperature range. Figure 1 shows a schematic of how a hypothetical material with several luminescent layers could work. The thickness of the layers needs to be carefully controlled in order to ensure that sufficient UV light is absorbed in each layer. The ALD technique exhibits excellent thickness control, and is thus particularly well suited for the fabrication of these materials.

While there may be TCS within each individual layer, there will be several NTCS that may be used for temperature sensing when considering the FIRs arising from the emission of the different layers. The emission ratio of NTCS is affected by several factors, such as particle size²⁻⁴, shape⁵, crystalline phase⁶⁻⁸, doping concentration⁹, and surrounding medium¹⁰. In layered samples, the luminescence is also affected by the thickness of the layers, and the order of the layers. As the thermal sensitivity depends on the luminescence intensity, there are consequently a wide range of parameters that can be used to further optimize the sensitivity for a specific temperature range.

In this study, we start by investigating how the emission in various single and dual layered YVO₄: Ln³⁺ (Ln = Nd, Sm, Eu, Dy, Ho, Er, Tm, Yb) thin films deposited by ALD is affected by temperature in the 300–850 K range. We then demonstrate how ALD can be used to make layered films that contain different luminescent ions and thus provide ratiometric temperature sensitive emission over a broad temperature range. The films can be deposited on a probe and attached to a surface, or alternatively deposited directly on the surface where the temperature is to be determined.

YVO₄ is a well-known host for lanthanides due to the strong absorption of (VO₄)³⁻, fairly low phonon energies, high transparency in the visible range, non-hygroscopicity, and a low symmetry Y₃⁺ site that can be substituted with lanthanides without distorting the structure²²⁻²⁴. As the films are only 100–150 nm thick, it is important that they are made of a highly absorbing material, and the films need to exhibit intense luminescence. Highly crystalline YVO₄ is thus considered an optimal host. With YVO₄ as host material, either temperature sensitive emission or excited state lifetimes have been reported for Eu³⁺²⁵, Dy³⁺¹⁰⁻¹ⁱ, Nd³⁺⁻²⁷⁻³⁰, and co-doped Er³⁺/Yb³⁺⁻³², or Er³⁺/Ho³⁺⁻³⁵. Previously, we determined that crystalline growth of YVO₄ can be achieved by using a 1-to-1 pulse ratio of Y(thd)₃/O₃ and VO(thd)₂/O₃ at 300 °C. The crystallinity, and as a consequence the luminescence intensity, can be further increased through post-deposition annealing¹¹. Hansen et al. have previously reported on the growth of most of the lanthanide oxides from Ln(thd)₃, enabling the doping of lanthanides by substituting some of the Y(thd)₃ pulses with other Ln(thd)₃ pulses.

Methods
The thin films investigated in this study were deposited with an F-120 research-type ALD-reactor (ASM Microchemistry Ltd) at 300 °C at a reactor pressure of ~3.6 mbar. The β-diketonate chelates Ln(thd)₃ (Ln = Nd, Sm, Eu, Dy, Ho, Er, Tm, Yb, thd = 2,2,6,6-tetramethyl-3,5-heptanediione) were used as the lanthanide precursors. Y(thd)₃, VO(thd)₂ and O₃ were used as the yttrium, vanadium and oxygen precursor, respectively. All information pertaining to the precursors is presented in Table 1. The concentration of the lanthanide doping relates to the amount of RE(thd)₃ that is being pulsed. The actual concentrations are not determined in this study and will be termed as pulse% RE(thd)₃, which will be abbreviated p% RE from here on. Previously, we have determined that
the relation between p% and mol% is approximately 1:2 at these pulsing levels and a deposition temperature of 300°C34, e.g. YVO4: 1 p% Dy3+ is expected to result in a Dy1+0.02Y0.98VO4 stoichiometry. Nitrogen was used as both carrier and purge gas and was supplied from gas cylinders (Praxair, 99.999%), run through a Mykrolis purifier, and maintained at a 300 cm3 min⁻¹ primary flow rate. All depositions were preceded by an in situ 10 min ozone cleaning consisting of 100 cycles of 1 s O3 pulse and 5 s N2 purge at the deposition temperature in order to remove any organic remains while letting the reactor stabilize its temperature.

Pulse durations were 3/3/3/3/3/3/3 s for all the RE(thd)3/purge/O3/purge/VO(thd)2/purge/O3/purge cycles. These are longer pulse and purge times than what would be required to achieve saturating conditions for all precursors35, but optimizing these parameters was not the focus of this study and it was thus kept constant for all precursors. Si (100) and SiO2 were used as substrates for the depositions. The thickness of the native oxide layer on the silicon substrates ranged from 3–20 nm and was measured by spectroscopic ellipsometry prior to each deposition.

The deposited films have a thickness between 100–145 nm, which previously was determined to be sufficient in order for (VO4)3− to absorb >90% of <300 nm light34. The samples are crystalline and luminescent as deposited, however, both these properties can be improved through post-deposition annealing above 700°C. For each deposition, a sample was annealed post deposition in air at 1000°C for 10 h. The graphs, images and figures in this study refers to annealed samples unless states otherwise.

The film thickness was determined with a J. A. Woollam alpha-SE ellipsometer in the 380–890 nm range. The Cauchy-model was used to parameterize the ellipsometry experimental data. Photoluminescence (PL) measurements in the visible range were performed with a 280 nm 1 mW diode and an OceanOptics USB4000 spectrometer+$ for the high-resolution measurements shown in the supplementary section, while an USB2000+ spectrometer with high sensitivity was used for all the spectra collected above 300 K presented in the paper. An OceanOptics NIR-Quest spectrometer was used for recording emission spectra in the 900–1700 nm NIR. The detectors were not calibrated with respect to each detectors wavelength dependent response, and while this affects the absolute FIR values, it does not affect the relative change in the FIR and consequently not the reported relative sensitivity.

The temperature sensitivity measurements were conducted by positioning the samples vertically inside a tube furnace and threading a quartz rod through a hole in the insulation. This setup allows photons to travel from the excitation source through a split fiber and then through the quartz rod aimed at the sample inside the furnace. The emitted light from the sample is passed back through the rod and the split fiber, before being collected at the spectrometer. A thermocouple was used to monitor the temperature inside the furnace. The resolution of the controller for the thermocouple was 1 K. The samples were heated to 700–875 K at a ramp rate of 2 K min⁻¹, and then kept at the max temperature for 10 min, before being cooled down by turning off the heater (ca. −0.5 K min⁻¹ on average).

The crystallinity of the samples was determined with a Bruker D8 Discovery X-ray diffractometer, using CuKα1 radiation and a Ge(111) monochromator. UV-Vis measurements were conducted on films deposited on fused silica in the range 200–900 nm with a Shimadzu UV-3600 instrument and an integrating sphere. A Hitachi SU8230 field emission scanning electron microscope (FE-SEM) was used to study the surface morphology of some of the samples.

### Results and Discussion

As only YVO4: Yb3+ had been previously deposited by ALD34, the first step in making multilayered films was to deposit YVO4 films doped with different lanthanides by ALD and to determine which of them are most promising for temperature sensing in multilayered films. The normalized emission spectra of all the deposited YVO4: Ln3+ (Ln3+ = Eu3+, Dy3+, Tm3+, Ho3+, Er3+, Sm3+, Nd3+, Yb3+) thin films after annealing are presented in Fig. 2a. Films with YVO4: 1 p% Tb3+ and YVO4: 1 p% Pr3+ were also prepared, but exhibited no detectable luminescence, which is to be expected since these ions easily oxidize to Tb4+ and Pr4+. The as-deposited samples are crystalline with a highly preferential orientation along the growth direction (shown for two samples in Fig S1) and exhibit luminescence. Their emission intensity is further improved by post-deposition annealing, which we previously have shown for YVO4: Yb3+ is due to increased crystallinity34,36. XRD data of the samples whose temperature

| Precursor | Producer | Purity | Sublimation temperature used [°C] | Pulse% cation/anion |
|-----------|----------|--------|----------------------------------|--------------------|
| VO(thd)2  | In-house | 130    | 50                               |                    |
| Y(thd)3   | In-house | 130    | 48–49                            |                    |
| Nd(thd)3  | Strem Chemicals | >98 % REO | 165 | 1 |
| Sm(thd)3  | Strem Chemicals | >98 % REO | 145 | 1 |
| Eu(thd)3  | Strem Chemicals | >98 % REO | 145 | 2 |
| Dy(thd)3  | Strem Chemicals | >98 % REO | 130 | 1 |
| Ho(thd)3  | Strem Chemicals | >98 % REO | 130 | 1 |
| Er(thd)3  | Strem Chemicals | >98 % REO | 135 | 1 |
| Tm(thd)3  | Strem Chemicals | >98 % REO | 130 | 1 |
| Yb(thd)3  | Volatec  | Not provided | 130 | 1 |
| O3        | In USA ozone generator (AC-2025) | >99.9% O2 | 100 | |

Table 1. Information on precursors used in this study.
sensing properties were determined in the present study is provided in Fig. S2. Individual emission spectra with peak labels for each ion is provided in Figs S3–10, which for YVO₄: Er³⁺ also includes emission in the 1450–1650 nm range. Transmission measurements of a selection of the samples are shown in Fig. S11, while photographs of samples exhibiting strong visible emission, including two dual layered samples, are presented in Fig. 2b.

Among the lanthanides whose emission is depicted in Fig. 2a, Eu³⁺, Dy³⁺, Er³⁺, Ho³⁺ and Nd³⁺ exhibit significant emission from TCS, enabling them to be used in ratiometric measurements. Kalinichev et al. previously performed a dedicated study on the temperature sensitivity of YVO₄: Nd³⁺ nanoparticles, where they investigated the intensity ratio between the 4F₃/2–4I₉/2 and 4F₅/2–2H₉/2–4I₉/2 transitions, finding sensitivities ranging from 9% K⁻¹ at 123 K, to 0.18% K⁻¹ at 873 K. The sensitivity in the lower temperature range is remarkable, however, the rapidly quenched luminescence means that the sensitivity is poor above 300 K. YVO₄: Nd³⁺ was consequently not investigated in the present study. Additionally, the YVO₄: Ho³⁺ sample was omitted from further investigations due to its fairly weak emission compared to other samples emitting in the visible range, and previously reported sensitivities for Ho³⁺ in ceramic glass are low (maximum of 0.1% K⁻¹).

To understand how the emission of the various lanthanides changes with temperature in YVO₄ thin films, a preliminary investigation was done where the total emission from the most emissive state of each sample was monitored in the 300–875 K range (Fig. 2c). The signal measured in this way is not referenced, so the results is merely an indication of the temperature range where the various lanthanides can be used as temperature sensors. YVO₄: Eu³⁺ emission has the highest quenching temperature, and should be included if the goal is to develop a sensor with high sensitivity above 600 K. In this study, we have first investigated single layer materials of two different lanthanides with TCS, before investigating two combinations of lanthanides suitable in the 473–773 K range.

**YVO₄: Er³⁺.** The visible range of the YVO₄: Er³⁺ emission spectrum is dominated by two peaks resulting from the ⁵H₁₁/₂–⁴I₁₅/₂ and the ⁴S₃/₂–⁴I₁₅/₂ transitions (for high-resolution spectrum see Fig. S6). The small energy gap separating these TCS causes significant overlap in their emission in most host structures, causing large detection errors. Nevertheless, Er³⁺ has been extensively studied for use as a temperature probe due to these TCS, though exclusively when co-doped with Yb³⁺ or Nd³⁺ as an upconversion phosphor, primarily for in vivo applications. Upconversion phosphors require high excitation power in order to perform, while regular phosphors can be easily excited by an inexpensive 1 mW UV-diode.

In the YVO₄: 1 p% Er³⁺ thin film presented in this study, the overlap between the emission from the ⁵H₁₁/₂–⁴I₁₅/₂ and the ⁴S₃/₂–⁴I₁₅/₂ transitions appear to be negligible when using detectors with high resolution. Figure 3a shows the thermal dependence of the emission from an YVO₄: 1 p% Er³⁺ thin film, using a detector with lower resolution, but higher sensitivity. The overlap is still small enough to not cause significant detection errors. The emission intensity, I, for each transition is proportional to the population of atoms in a given excited state at temperature T²:

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**Figure 2.** (a) Emission spectra of various lanthanides in YVO₄ thin films in the range 450–1410 nm. (b) Photographs of a selection of the annealed thin-films while being excited by a 280 nm diode. (c) The temperature dependence of the total measured emission intensity, resulting from emission from the most emissive state, for various lanthanides in YVO₄. Er1 and Er2 refer to emission from ²H₁₁/₂ and ⁴S₃/₂, respectively.
\[ I \propto g \alpha h \nu \exp \left( - \frac{E}{k_B T} \right), \]

where \( g \) is the degeneracy of the state, \( \alpha \) is the spontaneous emission rate, \( h \) is the Planck constant, \( \nu \) is the frequency, and \( E \) is the energy of the level. The FIR between two transitions assigned to the same phosphor, the lower level \( I_1 \) and upper level \( I_2 \), is taken as a measure of absolute temperature due to:

\[ \frac{I_2}{I_1} = \frac{g_a A_2 h \nu_2}{g_a A_1 h \nu_1} \exp \left( - \frac{\Delta E_{21}}{k_B T} \right) = C \exp \left( - \frac{\Delta E_{21}}{k_B T} \right), \]

where \( C \) is the temperature-independent scaling constant, and \( \Delta E_{21} \) is the energy gap between the two TCS. In \( \text{Er}^{3+} \), the \( ^4S_{3/2} \) state is considered the lower level, while the \( ^4I_{15/2} \) state is considered the upper level. \( \Delta E \) between two TCS can be obtained by fitting experimental data of the FIR to eq. 2, as shown for \( \text{YVO}_4: \text{Er}^{3+} \) in Fig. 3b. A good fit was achieved for the 300–660 K range \((r^2 = 0.9997)\), providing a fitted value for \( \Delta E \) of 623 cm\(^{-1}\), which is in good agreement with the emission spectra (ca. 650 cm\(^{-1}\)). The relative thermal sensitivity, \( S \), of the probe, defined as relative change in the FIR with temperature:

\[ S = \frac{\Delta \text{FIR}}{\Delta T} \cdot 100\%, \]

and is also shown in Fig. 3b. Note that the first derivative of the FIR gives a measure of the absolute sensitivity, and depends on the absolute FIR value, which as mentioned previously may depend on power density, particle size\(^{12,16}\), shape\(^{17}\), crystalline phase\(^{18,19}\), surrounding medium\(^{20}\), and in layered samples also the thickness of the layers and the order of the layers. Therefore, while the absolute sensitivity is relevant for the practical operation, it is not a meaningful parameter for comparison between probes, and thus only the relative sensitivities will be presented in this study. For the investigated temperature range, the \( S \) of this sample spans from 1.23% K\(^{-1}\) at 300 K to 0.21% K\(^{-1}\) at 660 K, making it reasonable for measuring temperature changes in e.g. water. The FIR between 295–370 K, and a picture of the experimental setup of \( \text{YVO}_4: 1 \text{p}\% \text{Eu}^{3+} \) film submerged in water, is given in Fig. S13. Due to the non-hygroscopicity of \( \text{YVO}_4 \), the \( \text{Eu}^{3+} \) emission is unaffected by water, which will be demonstrated for \( \text{YVO}_4: \text{Eu}^{3+} \) in the next section, and the resulting FIR is thus similar to that of Fig. 3b in the relevant temperature range.

**YVO\(_4\): Eu\(^{3+}\).** Eu\(^{3+}\) emission has previously been investigated for use as ratiometric temperature sensors in several hosts\(^{44-51}\), including \( \text{YVO}_4\)\(^{25}\). Previous studies have primarily investigated the thermal dependence of FIR between the emission from the \( ^5D_0 \) and \( ^5D_1 \), excited states. The study on \( \text{YVO}_4: \text{Eu}^{3+} \) investigated ratios between the emissions from two stark sublevels of the \( ^7F_2 \) excited state the 293–333 K range, with \( S \) being in the order of 0.1% K\(^{-1}\). As the emission from these two levels overlaps significantly (Fig. S3), in addition to the relatively poor reported sensitivity, it is evident that the FIR based on emission from these states is not well suited for use as a temperature sensor. In this study, we investigate the FIR between the emission of the \( ^3D_0 \rightarrow ^7F_2 \) transition and the \( ^5D_1 \rightarrow ^7F_2 \) transition.

The thermal dependence of the emission spectrum of \( \text{YVO}_4: 2 \text{p}\% \text{Eu}^{3+} \) is presented in Fig. 4a. While the \( ^5D_0 \rightarrow ^7F_2 \) emission is by far the strongest emission, it overlaps with both the emission from the \( ^3D_0 \rightarrow ^7F_4 \) and \( ^3D_1 \rightarrow ^7F_4 \) transitions, making accurate background subtraction challenging. Good agreement between heating and cooling measurements was obtained by instead using the intensity of the \( ^3D_0 \rightarrow ^7F_4 \) transition. Figure 4b shows the
The experimental data fitted to eq. 2 ($r^2 = 0.9994$). The average experimental value for $\Delta E$ was determined to be 1991 cm$^{-1}$, which is in good agreement with previous studies\(^45\). A lower $\Delta E$ (1872 cm$^{-1}$), which is closer to the experimental value suggested by the PL spectra (1735 cm$^{-1}$), is obtained by extracting $\Delta E$ from an Arrhenius-plot representation of the data, as shown in Fig. S14.

Figure 4b also shows the thermal dependence of $S$, which reaches a maximum of 0.59% K$^{-1}$ at 550 K. While $S$ is fairly low, it is still higher than e.g. YVO$_4$: Er$^{3+}$ in the 450–800 K range, making YVO$_4$: Eu$^{3+}$ a reasonable alternative for measurements in this temperature range. Discrepancies between heating and cooling are attributed to thermal mass in the system, and that the thermocouple used to measure the temperature was positioned 1–2 cm from the sample.

As YVO$_4$ is non-hygroscopic material, it will not absorb water, and submerging the films in water should thus not affect their luminescence. This was verified by submerging an YVO$_4$: 2 p% Eu$^{3+}$ sample in water for 60 hours while recording the PL emission. The total emission of the sample depends proportionally on the power of the excitation source, which fluctuates significantly over the course of such a long experiment. Changes in the background, in the atmosphere, or with the equipment is only expected to yield minor variations. Instability of the excitation source can be accounted for by recording the reflected UV signal (Fig. S15). Figure 4c shows how the total emission divided by the total reflected UV signal changes over the course of 60 hours while the sample is submerged in water. Fitting the data to a linear function shows that there is an insignificant increase in emission, and thus implies that the samples are completely unaffected by water. This enables monitoring of the temperature of transparent liquids inside e.g. sealed ampoules, Schlenk lines, or hydrothermal pressure vessels, provided there is an optical window that the signal can pass through. Note that underwater temperature sensing is not possible with IR thermometers due to the IR absorption of water, and that YVO$_4$ based temperature sensors thus provide a new solution to measuring in this condition.

Figure 4d,e shows two different screws, propped up with Al-foil during deposition, and coated with an as-deposited YVO$_4$: 2 p% Eu$^{3+}$ ALD-thin film, while being exposed to two different sources of UV light. Figure 4f shows the luminescence from the Al-foil used to keep the screws in place during deposition. The images demonstrate that it is possible to deposit luminescent YVO$_4$: Ln$^{3+}$ films on other surfaces than Si, glass or quartz. Heat conducting screws, clips, foils and similar items can also act as probes that can be attached to the desired area, in cases where direct deposition is inconvenient or impossible. Figure 4g shows the emission from an YVO$_4$: 2 p% Eu$^{3+}$ sample submerged in water. Note that it is also possible to cap ALD-films with a protective layer of Al$_2$O$_3$, or other transparent materials, in order to protect the coating from various chemical and physical environments.
Layered YVO₄: Eu³⁺/YVO₄: Dy³⁺. In addition to using two TCS on the same lanthanide, it is also possible to use the intensity ratio of two different lanthanides resulting from NTCS. In layered YVO₄: Eu³⁺/YVO₄: Dy³⁺, this results in at least six FIRs that can be extracted from the same signal. Both Eu³⁺ and Dy³⁺ exhibit two TCS, resulting in an additional four NTCS that can be used for temperature determination. A previous study on a similar system was recently performed by Wang et al. on SrWO₄: Eu³⁺, Dy³⁺ co-doped phosphor, yielding an impressive maximum $S_{\text{max}}$ of 1.71% K⁻¹ at 335 K when using the FIR between the 4I_{15/2}–6F_{15/2} emission of Dy³⁺ and the 5D₀–7F₂ emission of Eu³⁺ (FIR 1). (d) Thermal dependence of the FIR between the 575 nm ($F_{9/2}$–$H_{13/2}$) emission of Dy³⁺ and the 538 nm ($D_{0}$–$F_{2}$) emission of Eu³⁺ (FIR 2). (e) The thermal dependence of $S$ for the different FIRs in an YVO₄: 2 p% Eu³⁺/YVO₄: 1 p% Dy³⁺ thin film. FIR 1: 575 nm emission of Dy³⁺ and 700 nm emission of Eu³⁺ (green), FIR 2: 575 nm emission of Dy³⁺ and 538 nm emission of Eu³⁺ (blue), FIR 3: 700 nm and 538 nm emission of Eu³⁺ (red).

In the films investigated in the present study, the $F_{9/2}$–$H_{13/2}$ Dy³⁺ emission quenches quite abruptly in the 500–750 K range, while the Eu³⁺ emission quenches at a slower rate at these temperatures (Fig. 2c), resulting in high $S$ in this range. Figure 5a shows how the emission of an annealed sample with 39 nm YVO₄: 1 p% Dy³⁺ deposited on top of 78 nm YVO₄: 2 p% Eu³⁺ changes with temperature. A FE-SEM image of the surface of this sample is shown in Fig. 5b.

Note that while it has been demonstrated that the FIR methodology can still be used even when there is no thermal coupling between the involved states₆⁻¹¹, the number of possible excitation and de-excitation processes that affect the emission in these systems can be large. Finding an analytical solution to the rate equation system that describes the whole phenomena is consequently non-trivial. However, in order to determine $S$ for the system, it is only necessary that the data can be fitted by a function that adequately captures the changes in the experimental data. In previous studies on systems with NTCS, it was observed that all the FIRs presented an approximate exponential growth with the measured temperatures, similar to that of TCS. This suggests that the
same equations can be used to fit the data, despite the physical interpretation of each parameter being unclear. The FIR of the 575 nm (4F_{9/2} - 4H_{13/2}) emission of Dy^{3+} and 700 nm (4F_{5/2} - 4I_{9/2}) emission of Eu^{3+} (FIR 1) is presented in Fig. 5e. The best fit to eq. 1 is reasonable ($r^2 = 0.998$), and seems to capture the changes in the FIR well in the temperature sensitive 500–750 K range.

The ratio between the $4F_{9/2} - 4H_{13/2}$ transition of Dy$^{3+}$ and the $5D_{2} - 7F_{2}$ transition of Eu$^{3+}$ (FIR 2) is presented in Fig. 5d, and this data could also be fitted well to eq. 1 ($r^2 = 0.999$). The FIR that was used in YVO$_4$: Eu$^{3+}$, i.e. the ratio between the 538 nm and 700 nm emission of Eu$^{3+}$, is also present in this sample (FIR 3). The thermal dependence of this FIR is given in Fig. S17, and results in a slightly lower $S$ compared to a sample without any Dy$^{3+}$.

The thermal dependence of $S$ of the three different FIRs in the layered YVO$_4$: 2 p% Eu$^{3+}$/YVO$_4$: 1 p% Dy$^{3+}$ thin film is presented in Fig. 5e. The addition of an YVO$_4$: Dy$^{3+}$ layer on top of YVO$_4$: Eu$^{3+}$ enhances $S$ significantly in the 500–750 K range, with a maximum of 3.6% K$^{-1}$ at 640 K. The FIR resulting from TCS on Dy$^{3+}$ is not included in Fig. 5e, but exhibits $S$ of 0.9–1.8% K$^{-1}$ below 400 K, enabling high $S$ over the entire 300–800 K range.

A list of phosphor materials that can be used for temperature detection above 473 K, and their $S_{\text{max}}$ and operating temperature range (within limits of measurement) for selected phosphors that can operate above 473 K is presented in Table 2. It is challenging to make a useful comparison between various systems based on $S_{\text{max}}$ due to the differences in operating range. While the listed systems still exhibit luminescence above 473 K, their $S_{\text{max}}$ may be at a much lower temperature, and the sensitivity in the 473–750 K range may be significantly lower than the value listed. E.g. the $S_{\text{max}}$ observed for the YVO$_4$: Er$^{3+}$ film presented in this study was 1.2% K$^{-1}$ at 300 K, while above 473 K, $S$ is less than 0.5% K$^{-1}$ and gradually decreasing, resulting in an average $S$ of only 0.30% K$^{-1}$ in the 473–673 K range. On the other hand, the dual-layer YVO$_4$: Eu$^{3+}$/YVO$_4$: Dy$^{3+}$ thin film has an average $S$ of 2.2% K$^{-1}$ over the 475–750 K range (2.4% in the 500–750 K range). An average sensitivity over a certain operating range would be more sensible to compare, though such numbers have not been compared in previous studies, as such comparisons only make sense if the systems are compared for use in a specific application requiring a certain operating range. A recent study on the Pr$^{3+}$: Y$_2$Ti$_2$O$_7$ system, using the FIR of host trap emission and the $5D_{2} - 7F_{2}$ emission of Pr$^{3+}$, demonstrated an impressive $S_{\text{max}}$ of 5.25% K$^{-1}$ at 288 K in the operating range 289–573 K. However, above 473 K it is less than 1.5% K$^{-1}$ and decreasing, clearly making it less suitable than the dual layer YVO$_4$: Eu$^{3+}$/YVO$_4$: Dy$^{3+}$ thin film in the 500–750 K range. To the authors’ knowledge, there are no previously investigated materials that exhibit higher average $S$ than that of the dual layer YVO$_4$: Eu$^{3+}$/YVO$_4$: Dy$^{3+}$ presented in this study for FIR measurements in the 500–750 K temperature range, making this currently the most attractive material for non-contact temperature sensing in this range.

**Layered YVO$_4$: Tm$^{3+}$/YVO$_4$: Eu$^{3+}$.** YVO$_4$: Tm$^{3+}$/YVO$_4$: Eu$^{3+}$ is another dual layered material that seemed promising based on Fig. 2c. YVO$_4$: Tm$^{3+}$ quenches at a slower rate, but over a slightly broader temperature range compared to YVO$_4$: Dy$^{3+}$. The emission spectra in the 300–850 K temperature range of a dual layered thin film consisting of 20 nm YVO$_4$: 2 p% Eu$^{3+}$ deposited on top of 125 nm YVO$_4$: 1 p% Tm$^{3+}$ is presented in Fig. 6a, while a FE-SEM image of the surface of the sample is provided in Fig. 6b. The strong Eu$^{3+}$ emission indicates that the large difference in thickness between the Eu$^{3+}$ and Tm$^{3+}$ layer is required for a balanced ratio of the emission intensity. It has previously been determined that there is resonant energy transfer from Tm$^{3+}$ to Eu$^{3+}$, and thus the emission properties will be dominated by Eu$^{3+}$ when mixed together. By making a layered structure, the energy transfer from Tm$^{3+}$ to Eu$^{3+}$ can be reduced, enabling intense emission from both lanthanides.

In the YVO$_4$: Tm$^{3+}$, Eu$^{3+}$ system there are at least three FIRs suitable for temperature measurements. The FIR of the $3G_{4} - 2H_{6}$ transition of Tm$^{3+}$ and $5D_{0} - 7F_{2}$ of Eu$^{3+}$ is presented in Fig. 6c (FIR 1). It is evident that the FIR increases exponentially, and the best fit to eq. 2 is a reasonable ($r^2 = 0.998$), indicating that this is indeed a valid approach for this system as well. The FIR of the $3G_{4} - 2H_{6}$ transition of Tm$^{3+}$ and $5D_{2} - 7F_{2}$ transition of Eu$^{3+}$ is presented in Fig. 6d (FIR 2), while the FIR of the $5D_{0} - 7F_{2}$ and the $5D_{2} - 7F_{2}$ transition of Eu$^{3+}$ in this sample (FIR 3) is provided in Fig. S18. Figure 6e shows a comparison between the thermal dependence of $S$ of the three FIRs. FIR 2 exhibits a maximum $S$ of 1.9% K$^{-1}$ at 675 K, and displays a reasonable sensitivity over the 500–775 K range (average $S$ = 1.35% K$^{-1}$). S is lower compared to YVO$_4$: Dy$^{3+}$/YVO$_4$: Eu$^{3+}$, but the operating range is slightly broader.

### Table 2. The maximum relative sensitivities, $S_{\text{max}}$, and operating temperature range (within limits of measurement) for selected phosphors that can operate above 473 K.

| System | Transitions | $S_{\text{max}}$ [% K$^{-1}$] | Range [K] | Source |
|--------|-------------|-----------------|-----------|--------|
| YVO$_4$: Er$^{3+}$ | $9_{11/2} - 9_{13/2}$ / $S_{31/2} - 9_{11/2}$ | 1.2 | 300–675 | This work |
| YVO$_4$: Eu$^{3+}$ | $3D_{2} - 7F_{5/2}$ / $5D_{0} - 7F_{2}$ | 0.6 | 300–800 | This work |
| YVO$_4$: Dy$^{3+}$ | $9_{11/2} - 9_{13/2}$ / $S_{31/2} - 9_{11/2}$ | 1.8 | 298–673 | 24 |
| YVO$_4$: Eu$^{3+}$, Dy$^{3+}$ | Eu$^{3+}$: $5D_{0} - 7F_{2}$ / Dy$^{3+}$: $5D_{0} - 7F_{2}$ | 3.6 | 500–750 | This work |
| YVO$_4$: Eu$^{3+}$, Dy$^{3+}$ | Eu$^{3+}$: $5D_{0} - 7F_{2}$ / Dy$^{3+}$: $5D_{0} - 7F_{2}$ | 3.0 | 500–750 | This work |
| YVO$_4$: Tm$^{3+}$/Eu$^{3+}$ | Tm$^{3+}$: $5G_{4} - 2H_{6}$ / Eu$^{3+}$: $3D_{2} - 7F_{2}$ | 1.9 | 500–775 | This work |
| Y$_2$O$_3$: Er$^{3+}$ nanoparticles | $9_{11/2} - 9_{13/2}$ / $S_{31/2} - 9_{11/2}$ | 1.5 | 298–500 | 23 |
| Tb$^{3+}$/Pr$^{3+}$/NaLu(WO$_4$)$_2$ | $9_{13/2} - 9_{15/2}$ / $S_{3/2} - 9_{15/2}$ | 1.45 | 583–783 | 23 |
| Gd:Ho$^{3+}$ | $5I_{5} - 4F_{7/2}$ / $G_{4} - 5I_{5}$ | 0.1 | 303–643 | 23 |
| 3NaYF$_4$: Nd$^{3+}$ | $9_{13/2} - 9_{15/2}$ / $S_{3/2} - 9_{15/2}$ | 1.1 | 323–673 | 37 |
| La$_2$O$_3$: Yb$^{3+}$, Nd$^{3+}$ | $9_{13/2} - 9_{15/2}$ / $S_{3/2} - 9_{15/2}$ | 1.4 | 300–1200 | 4 |
| Dual phase GC: Cr$^{3+}$/YVO$_4$: Eu$^{3+}$ | $8_{3/2} - 6I_{15/2}$ / $8_{1/2} - 6I_{15/2}$ | 0.6 | 300–573 | 15 |

*Derived from FIR data.
Conclusion
In this study, controlled deposition of luminescent YVO₄: Ln³⁺ (Ln = Nd, Sm, Eu, Dy, Ho, Er, Tm, Yb) by ALD was achieved, both as single layers and as multilayers, and the thermal dependence of the photoluminescence in the 300–875 K range of the samples doped with Eu³⁺, Dy³⁺, Tm³⁺, Sm³⁺, Er³⁺ and Yb³⁺ was investigated. FIR measurements using TCS on Er³⁺ and Eu³⁺ demonstrated maximum sensitivities reaching 1.2% K⁻¹ for YVO₄: Er³⁺ at 300 K, and 0.6% K⁻¹ for Eu³⁺ at 575 K. FIR measurements were also performed using excited states situated on different lanthanides in layered YVO₄: Eu³⁺/YVO₄: Dy³⁺ and YVO₄: Tm³⁺/YVO₄: Eu³⁺. The dual layered materials exhibit a $S_{\text{max}}$ of 3.6% K⁻¹ at 640 K, with $S$ significantly improved in the whole 500–775 K range compared to the single layer YVO₄: Eu³⁺ thin film, and also compared to any other previously investigated materials in this range. The dual layered films are particularly attractive for use in boreholes where the temperatures exceed 500 K. The films were successfully deposited on all tested surfaces (Si, Fe, Al, glass, quartz, and steel), indicating that they can be applied to most industrially relevant surfaces. It was also demonstrated that the luminescence of the films is unaffected by water, which enables monitoring of the temperature of transparent liquids inside e.g. sealed ampoules, Schlenk lines or hydrothermal pressure vessels. The study shows that it is possible to make highly customizable, chemically and physically robust coatings by ALD that can provide ratiometric temperature sensing over a broad temperature range and with high sensitivity.

Data Availability
The experimental data is available upon request or can be accessed from the Zenodo repository.

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