Excited-state absorption thermometry as a pathway to unlock high sensitivity

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As the foremost thermodynamic state variable, the precise measurement of temperature holds increasing significance in state-of-the-art technologies, such as the processing capabilities of networked devices[1]. Over the years, advancements in temperature measurement have been manifold, with remote temperature sensing via luminescence thermometry (LT) currently in the spotlight among the available methods. In LT, temperature-induced changes in the spectroscopic properties of an ensemble of probes is harnessed to output a thermal readout[1]. However, a recently raised caveat in the literature is: *which property and/or strategy should be used in LT*? Exploring new strategies and thermal dependencies may push the field of LT toward unforeseen limits. Mindful of this interplay, using excited-state absorption (ESA) in LT falls within deeply unexplored strategies, as only a handful of works have dealt with this plan-of-action[2]. In this context, two proof-of-concept phosphors, i.e., $GdYO_3:Eu^{III}$(1-9at.%) and $GdYO_3:Eu^{III}$(1-9at.%),Al^{III}(3at.%) were synthesized by an adapted Pechini method at 1100 °C/5 h under an air atmosphere. X-ray diffraction (XRD) analysis exhibited the single-phase formation of $GdYO_3$ host, enabling the photophysical investigation of the phosphor. At room temperature, the 7%-Eu^{III} phosphor excelled among all samples, while the 9%-Eu^{III},3%-Al^{III} sample displayed the highest relative emission intensity among the Al^{III}-codoped phosphors. Hence, from now on these samples are labelled as 7Eu and 9EuAl, respectively. Accordingly, emission spectra in the 77 – 500 K temperature range under 464 nm ($^5D_2 \leftarrow {}^7F_0$) and 532 nm ($^5D_1 \leftarrow {}^7F_1$) excitation were recorded. The ratio between the $^5D_0 \rightarrow {}^7F_2$ (612 nm) emission band under both excitations was used as a thermometric parameter. It is noteworthy that this strategy is only possible due to the presence of thermally coupled $^7F_0$ and $^7F_1$ levels, since at high temperatures, the population of $^7F_1$ increases. Interestingly, the highest relative sensitivity (S_r) assumed values of 2.02% K^{-1} and 2.52% K^{-1}, respectively, for the 7Eu and 9EuAl samples, close to the cryogenic temperature of 77 K. Although these thermometers adhered to the conventional Boltzmann behavior due to the high thermal coupling between $^7F_{0,1}$, they exhibited S_r values higher than those of commonly studied Boltzmann thermometers[2], symbolizing notable progress. The thermal resolution problem poses a meaningful query in LT. However, both thermometers displayed temperature uncertainties (δT) below 0.05 K close to 77 K, whereas the highest δT assumed values near 0.15 K at 500 K. This finding implies high thermal resolution, and, when combined with the desired S_r values, highlight the potential of this strategy. Overall, this work underscores that scratching only the surface of a combination of plan-of-action and materials design may unlock the potential of luminescent thermometers towards high sensitivities.

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References

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