

Improving excited-state absorption thermometry in lanthanide(III)-based materials via advanced data analysis algorithms

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Highlights

Temperature-induced changes in the spectroscopic properties of probes as a thermal sensor
Multiple excited-state absorption pathways unlock thermal sensing via multiple parameters
Sophisticated data analysis algorithm to treat the thermometric essay enhances sensitivity by five-fold

Abstract

The utmost importance in remote temperature measurements has been driving the development of advanced sensing techniques, where luminescence thermometry (LT) is particularly suitable for measuring temperatures at the submicron scale¹. LT operates by correlating temperature-induced changes in the spectroscopic properties of probes with thermal readouts¹. However, a recently raised query in the literature is: *which property and/or strategy should be used in LT?* This question is driven by distinct thermal outputs generated when different luminescent features are employed. Aware of this interplay, attention has been drawn toward single-band thermometry, which is often performed through excited-state absorption (ESA)². This is a consequence of the limited number of thermometric parameters with ESA, thereby reducing the reliance on trial-and-error approaches when evaluating multiple parameters. Thus, enhancing the performance of ESA-based single-band thermometers is promising and can be achieved through data analysis algorithms, presenting an unexplored avenue that advances the field of LT. In this context, this study surveyed the potential of non-negative matrix factorization (NMF) for ESA thermometry. The NMF algorithm uncovers patterns hidden among the data by integrating explanatory variables into a single block to forecast an outcome. For this aim, proof-of-concept phosphors, i.e., GdYO₃:Eu^{III}(1-9at.%) and GdYO₃:Eu^{III}(1-9at.%)Al^{III}(3at.%) were synthesized by an adapted Pechini route at 1100 °C/5 h. The structure of the phosphor in the absence of spurious phases was confirmed by powder x-ray diffraction (PXRD) analysis. Simultaneously, temperature dependent emission spectra at the 77 – 500 K range were acquired for 7%-Eu^{III} and its analog, 7%-Eu^{III},Al^{III}, labeled as 7Eu and 7EuAl, respectively. The samples were excited at 464 nm (⁵D₂←⁷F₀), 532 nm (⁵D₁←⁷F₁) and 586 nm (⁵D₀←⁷F₁). As a consequence of the thermal coupling between ⁷F₀ and ⁷F₁ levels, the ratio between the ⁵D₀→⁷F₂ (612 nm) emission band under each excitation was used to evaluate thermal changes, resulting in three distinct thermometric parameters, Δ_{J/J}, defined as: Δ_{1/2} (532/464), Δ_{0/2} (586/464), and Δ_{1/0} (586/532). Among these, Δ_{0/2} presented the highest relative sensitivity (S_r), with values of 2.02% K⁻¹ (7Eu) and 2.52% K⁻¹ (7EuAl) near the liquid nitrogen temperature of 77 K. It is noteworthy that the thermal uncertainties (δT) of both thermometers were maintained below 0.05 K near 77 K, with the highest values approaching 0.15 K at 500 K. By using the NMF algorithm, the three thermometric parameters were integrated into a unified parameter, which was used to retrieve the relative thermal sensitivity of 10.1% K⁻¹ (7Eu) and 12.3% K⁻¹ (7EuAl), representing up to a five-fold increase. These high sensitivities were combined with low uncertainties, which were maintained below 0.05 K for both thermometers using NMF. Therefore, this study demonstrates that improved performance can be harvested by combining material design and data analysis, thereby setting the stage for using sophisticated methods to treat ESA thermometric essays.

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