Multimode high-sensitive optical YVO₄:Ln³⁺ nanothermometers (Ln³⁺ = Eu³⁺, Dy³⁺, Sm³⁺) using charge transfer band features

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Multimode high-sensitive optical $\text{YVO}_4\text{:Ln}^{3+}$ nanothermometers ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}$) using charge transfer band features

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ABSTRACT

Accurate thermal sensing with good spatial resolution is currently required in variety of scientific and technological areas. Luminescence nanothermometry has shown competitive superiority for contactless temperature sensing especially at the nanoscale. To broaden use of such thermometers, development of novel sensor type with high sensitivity and resolution is highly demanded. Herein, we report single-phase Ln^{3+} -doped YVO_4 nanophosphors synthesized via modified Pechini method as multimode optical thermometers with wide-range temperature probing (299–466 K). The observed temperature-induced red shift of charge transfer band was utilized to provide thermal sensing. Temperature sensing was based on luminescence intensity ratio using emission intensities obtained upon charge transfer band and direct lanthanide excitation, spectral position of charge transfer band and its bandwidth. The suggested probing strategies provided high relative thermal sensitivity (up to 3.09 % K^{-1}) and precise temperature resolution (up to 0.1 K). The obtained results can be useful for design of novel contactless luminescence thermometers.

1. INTRODUCTION

Temperature measurements are of great importance in variety of scientific and industrial applications allowing temperature sensors to occupy 80% of the worldwide sensor market¹. Rapid development of nanotechnology in recent decade resulted in shift of attention to nanoscale, especially for biological and medical application as well as for integral optics and microelectronics, where traditional contact thermometers cannot be used^{2–4}. Therefore, contactless thermometers with submicron spatial and sub-degree temperature resolution are in high demand.

One of the most promising non-contact thermal sensors are optical thermometers utilizing various luminescence features as temperature dependent parameters^{5–7}. Nowadays, luminescence thermometry based on emission line intensity (or ratio between two emission lines), spectral line position, bandwidth, rise or decay lifetime of excited level or polarization are used^{8–10}. The most typical technique utilizes temperature induced change of luminescence intensity ratio (LIR) of two thermally coupled energy levels^{11–13}. However, this approach has intrinsic limitation of relative thermal sensitivity (S_r), which is connected with maximal energy gap between thermally coupled levels (2000 cm^{-1})¹⁴. To enhance sensitivity, this energy gap should be as much as possible, but, if energy difference is overlarge, thermal coupling will be lost resulting in a decreased S_r value¹⁵. The best sensitivities using thermally coupled energy levels based method were achieved for Nd^{3+} ($^4\text{F}_{7/2}$ and $^4\text{F}_{3/2}$ levels)^{16,17} and Eu^{3+} -doped ($^5\text{D}_1$ and

5D_0 levels)¹⁸ thermometers. To overcome aforementioned limitation, many scientific groups have developed novel sensing techniques. For example, luminescence thermometry based on dual emitting centers^{19–21}, metal-to-metal intervalence charge transfer state^{22,23}, and thermal population of lower-lying excited energy levels²⁴ have been successfully demonstrated. Recently, Zhou et al. reported temperature induced shift of the charge transfer band (CTB) edge in rare earth ions doped vanadates and proposed promising sensing strategy based on different thermal behavior of emission line intensity upon host excitation (near CTB tail) and direct excitation of rare earth ion^{25,26}. Herein, we studied applicability of this LIR-based thermal sensing strategy for Ln^{3+} -doped YVO_4 ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}$) nanoparticles. Moreover, we suggest to utilize spectral line position and bandwidth of CTB as temperature dependent parameters, which make Ln^{3+} -doped YVO_4 phosphors promising multimode thermal sensors. All regarded sensing strategies were compared in terms of thermometric performances (relative thermal sensitivity and temperature resolution).

2. EXPERIMENTAL

Ln^{3+} -doped YVO_4 nanocrystalline powders ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}$) were prepared via modified Pechini method, which has been previously used for synthesis of various oxides systems activated by rare earths ions^{27–29}. The prepared samples were studied in the powder form. X-ray diffraction patterns were measured with Rigaku «Miniflex II» diffractometer with CuK_α -radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 15° to 60° . Phase identification was performed using a powder diffraction database PowderDiffractionFile (PDF-2, 2011). Scanning electron micrograph (SEM) images were obtained using SUPRA 40VP WDS scanning electron microscope. Photoluminescence properties were studied with modular fluorescence spectrometer Fluorolog-3 equipped with xenon lamp as an excitation source. Temperature experiments were carried out on the same spectrometer equipped with optical fibers and heating stage controlled with ThorLabs TC200 with a resolution of 0.1°C .

3. RESULTS AND DISCUSSION

3.1 Structure and morphology of Ln^{3+} -doped YVO_4 NPs

Phase composition of synthesized YVO_4 nanoparticles (NPs) doped with different lanthanides were studied using X-ray Powder Diffraction. XRD patterns of $\text{YVO}_4:\text{Eu}^{3+}$ 1 at.%, $\text{YVO}_4:\text{Dy}^{3+}$ 1 at.%, $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% samples as well as standard YVO_4 card (tetragonal phase, space group $I4_1/amd$, JCPDS 17-0341) are shown in Figure 1a. As can be seen, all diffraction peaks of powders correspond to tetragonal phase. So, we can conclude that chosen synthesis procedure results in formation pure phase phosphors without crystalline impurities. As all $\text{YVO}_4:\text{Ln}^{3+}$ samples were prepared under the same synthesis conditions, so particle size should be also the same. Figure 1b presents the scanning electron microscopy image of the $\text{YVO}_4:\text{Eu}^{3+}$ 1 at. % phosphor. One can see that powder is composed from weakly agglomerated NPs with average size of 70–80 nm.

Figure 1. (a) XRD pattern of $\text{YVO}_4:\text{Eu}^{3+}$, $\text{YVO}_4:\text{Dy}^{3+}$ and $\text{YVO}_4:\text{Sm}^{3+}$ nanoparticles and standard card of YVO_4 (JSPDS 17-0341); (b) SEM image of $\text{YVO}_4:\text{Eu}^{3+}$ 1 at.% nanoparticles.

3.2 Luminescence thermal sensing using $\text{YVO}_4:\text{Eu}^{3+}$ NPs

Figure 2 presents steady-state photoluminescence properties of $\text{YVO}_4:\text{Eu}^{3+}$ 1 at.% sample measured at different temperatures between 299 and 466 K. Excitation spectra (Figure 2a) monitored forced electric dipole transition $^5\text{D}_0\text{--}^7\text{F}_2$ (619 nm). It includes intense UV broad band centered at about 300 nm, which can be assigned to the charge transfer from the oxygen ligands to the central vanadium atom inside the VO_4^{3-} ion and to the charge transfer transition between Eu^{3+} and O^{2-} ^{30,31}, and several weak sharp lines corresponding to the typical intra-configurational transitions inside Eu^{3+} ion: $^7\text{F}_0\text{--}^5\text{D}_4$ (362 nm), $^7\text{F}_0\text{--}^5\text{L}_7$ (382 nm), $^7\text{F}_0\text{--}^5\text{L}_6$ (395 nm), $^7\text{F}_0\text{--}^5\text{D}_3$ (417 nm), $^7\text{F}_0\text{--}^5\text{D}_2$ (465 nm), $^7\text{F}_1\text{--}^5\text{D}_2$ (474 nm), $^7\text{F}_2\text{--}^5\text{D}_2$ (490 nm), $^7\text{F}_0\text{--}^5\text{D}_1$ (527 nm), $^7\text{F}_1\text{--}^5\text{D}_1$ (537 nm), and $^7\text{F}_1\text{--}^5\text{D}_0$ (593 nm). Noteworthy, temperature increase leads to sufficient red shift of charge transfer band, whereas spectral position of transitions inside Eu^{3+} ion stay unchanged. Emission spectra $\text{YVO}_4:\text{Eu}^{3+}$ 1 at.% sample at different temperatures obtained upon 350 and 395 nm excitation are shown in Figure 2b and 2c, respectively. These spectra consist of narrow lines attributed to the electron transitions inside 4f shell of Eu^{3+} ions. The most intense bands are originated from $^5\text{D}_0$ metastable level: magnetic dipole $^5\text{D}_0\text{--}^7\text{F}_1$ transition (594 nm), electric dipole $^5\text{D}_0\text{--}^7\text{F}_2$ transition (615 and 619 nm), $^5\text{D}_0\text{--}^7\text{F}_3$ transition (652 nm), and electric dipole $^5\text{D}_0\text{--}^7\text{F}_4$ transition (698 and 704 nm). However, emission from higher excited level was also observed: $^5\text{D}_2\text{--}^7\text{F}_6$ (609 nm).^{32,33}

Figure 2. (a) Excitation spectra of $\text{YVO}_4:\text{Eu}^{3+}$ 1 at.% nanoparticles measured at different temperatures ($\lambda_{\text{em}} = 619$ nm); emission spectra of $\text{YVO}_4:\text{Eu}^{3+}$ 1 at.% nanoparticles measured at different temperatures upon (b) $\lambda_{\text{ex}} = 350$ nm and (c) $\lambda_{\text{ex}} = 395$ nm.

Emission intensity upon 350 and 395 nm excitation demonstrated opposite temperature behavior. Red shift of CTB resulted in monotonic intensity growth for 350 nm excitation, while thermal quenching led to gradual decline of emission intensity in case of 395 nm excitation. Opposite temperature behavior of luminescence intensity upon different excitation wavelength gives an opportunity to provide thermal sensing using ratiometric technique by monitoring ratio between intensity of the chosen band obtained under 350 and 395 nm excitation. Ratiometric approach provides better sensing accuracy comparing with single band intensity approach due to independence on measurement conditions such as excitation power fluctuations or sample amount¹⁴.

To check the suggested strategy, we monitored the most prominent Eu^{3+} transitions: $^5\text{D}_0\text{--}^7\text{F}_1$, $^5\text{D}_0\text{--}^7\text{F}_2$ and $^5\text{D}_0\text{--}^7\text{F}_4$. LIRs were calculated based on integral intensities because of better results comparing with point values³⁴. Figure 3a displays evolution of LIR^{619} as a function of temperature for $\text{YVO}_4\text{:Eu}^{3+}$ 1 at.%, whereas Figure S1 and S2 presents evolution of LIR^{594} and LIR^{698} , respectively. Similar to LIR of two thermally coupled levels, we fitted the obtained experimental data with Boltzmann equation:

$$\text{LIR} = \frac{I_{\text{ex}350}}{I_{\text{ex}395}} = A \exp\left(-\frac{\Delta E}{kT}\right) \quad (1)$$

where A is temperature independent constant, defined purely by the material properties, ΔE is the effective energy gap, and $k=0.695 \text{ cm}^{-1} \text{ K}^{-1}$ is the Boltzmann constant. The approximation function was chosen due to its simplicity and fitting accuracy, but it does not have the same deep physical meaning as in case of LIR between two thermally coupled levels. Adj. R^2 values were better than 0.99 for all approximations. An effective gap ΔE obtained from Eq. 1 was determined to be independent on monitoring emission band: $1390 \pm 58 \text{ cm}^{-1}$ (619 nm), $1439 \pm 63 \text{ cm}^{-1}$ (594 nm), and $1416 \pm 58 \text{ cm}^{-1}$ (698 nm).

Excitation spectra of $\text{YVO}_4\text{:Eu}^{3+}$ 1 at.% NPs measured at different temperatures clearly displayed red shift of CTB along with temperature increase. Temperature-induced shift of excitation band is a result of two main factors. First, the electronic energy level of the charge transfer state usually tends to shift toward lower energy upon increasing temperature caused by the thermal expansion. So, the energy difference between the lowest charge transfer state and the ground state decreases, which leads to red shift of excitation band. Second, the thermal population of vibrational sublevels of the ground electronic energy level results in a reduction of excitation energy, i.e., red shift of the CTB. Besides, the temperature-induced broadening of the CTB also contributes the red shift of the excitation band edge²⁵.

Except LIR, other luminescence parameters can be used as temperature dependent to provide contactless optical thermal sensing⁹. As it was observed, temperature increase results in sufficient red shift and broadening of charge transfer band at excitation spectrum of $\text{YVO}_4\text{:Eu}^{3+}$ 1 at.% NPs. So, the spectral line position and bandwidth of charge transfer band were tested for thermometry purposes. As can be seen from Figure 2a, charge transfer band has complex line shape. Therefore, deconvolution procedure was performed to obtain spectral parameters of its components. Noteworthy, charge transfer band was fitted by two **Gaussian profiles**, and the longer wavelength one was utilized for thermal sensing. Examples of deconvolution procedure at different temperatures are provided in Supplementary Information (Figure S3). Temperature evolutions of spectral line position and full width at half maximum (FWHM) of $\text{YVO}_4\text{:Eu}^{3+}$ 1 at.% charge transfer band are shown in Figure 3b and Figure 3c, respectively. Both experimental dependences demonstrated pseudo-linear behavior, which facilitates practical application of such parameters for thermal sensing.

Figure 3. Evolution of (a) LIR⁶¹⁹, (b) spectral line position and (c) FWHM as a function of temperature for YVO₄:Eu³⁺ 1 at.% nanoparticles.

3.3 Luminescence thermal sensing using YVO₄:Dy³⁺ NPs

Photoluminescence properties of YVO₄:Dy³⁺ 1 at.% sample measured within 299–466 K temperature range are shown in Figure 4. Excitation spectra (Figure 4a) monitored forced electric dipole transition ⁴F_{9/2}–⁶H_{13/2} (572 nm). It consists of intense UV broad band centered at about 300 nm, which can be assigned to the charge transfer from the oxygen ligands to the central vanadium atom inside the VO₄³⁻ ion and several weak narrow lines in visible region. Low-intensity peaks, not easily visible in Figure 4a, are attributed to the typical intra-configurational transitions inside Dy³⁺ ion: ⁶H_{15/2}–⁴I_{13/2} (390 nm), ⁶H_{15/2}–⁴G_{11/2} (427 nm), ⁶H_{15/2}–⁴I_{15/2} (449 and 453 nm) and ⁶H_{15/2}–⁴F_{9/2} (473 nm). As in case of YVO₄:Eu³⁺ nanophosphor, temperature increase significantly affects charge transfer band.

Emission spectra of YVO₄:Dy³⁺ 1 at.% sample at different temperatures obtained upon 350 and 390 nm excitation are presented in Figure 4b and 4c, respectively. These spectra consist of narrow lines assigned to the electron transitions inside 4f shell of Dy³⁺ ions. Almost all bands are originated from ⁴F_{9/2} metastable level: ⁴F_{9/2}–⁶H_{15/2} (482 nm), ⁴F_{9/2}–⁶H_{13/2} (572 nm), and ⁴F_{9/2}–⁶H_{11/2} (662 nm), however, emission from higher excited level is also present: ⁴I_{15/2}–⁶H_{15/2} (455 nm).

Figure 4. (a) Excitation spectra of YVO₄:Dy³⁺ 1 at.% nanoparticles measured at different temperatures (λ_{em} = 572 nm); emission spectra of YVO₄:Dy³⁺ 1 at.% nanoparticles measured at different temperatures upon (b) λ_{ex} = 350 nm and (c) λ_{ex} = 390 nm.

All previously described strategies of optical thermal sensing were implemented for YVO₄:Dy³⁺ 1 at.% NPs. LIRs were calculated between integral intensities of the most prominent Dy³⁺ transitions (⁴F_{9/2}–⁶H_{15/2} (572 nm) and ⁴F_{9/2}–⁶H_{13/2} (482 nm)) obtained upon 350 and 390 nm excitation. Figure 5a shows temperature dependence of LIR⁵⁷² for YVO₄:Dy³⁺ 1 at.%, while Figure S4 presents evolution of LIR⁴⁸². Both experimental data sets were well fitted by Eq. 1, giving similar effective gap ΔE of 1473±63 cm⁻¹ (572 nm) and 1489±66 cm⁻¹ (482 nm).

Figure 5b and 5c display evolution of spectral line position and FWHM of $\text{YVO}_4:\text{Dy}^{3+}$ 1 at.% charge transfer band as a function of temperature. Both luminescence parameters were obtained from deconvolution procedure. The observed linear trends can be easily used for thermal sensing in regarded temperature range.

Figure 5. Evolution of (a) LIR^{572} , (b) spectral line position and (c) FWHM as a function of temperature for $\text{YVO}_4:\text{Dy}^{3+}$ 1 at.% nanoparticles.

3.4 Luminescence thermal sensing using $\text{YVO}_4:\text{Eu}^{3+}$ NPs

Figure 6a presents excitation spectra of $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% sample measured at different temperatures ranging from 299 to 466 K. These spectra, monitored forced electric dipole transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (646 nm), are composed from intense UV broad band centered at about 300 nm, which can be assigned to the charge transfer from the oxygen ligands to the central vanadium atom inside the VO_4^{3-} ion and several weak narrow lines at longer wavelength, which corresponds to the typical intra-configurational transitions inside Sm^{3+} ion: $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$ (407 nm), $^6\text{H}_{5/2} \rightarrow ({}^6\text{P}, {}^4\text{P})_{5/2}$ (421 nm), $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{9/2}$ (442 nm), $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{13/2}$ (467 nm), $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}$ (475 and 479 nm), and $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{7/2}$ (502 nm). Similarly to $\text{YVO}_4:\text{Eu}^{3+}$ and $\text{YVO}_4:\text{Dy}^{3+}$ cases, temperature growth most noticeably affects charge transfer band.

Figure 6b and 6c show emission spectra of $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% NPs at different temperatures measured upon 350 and 407 nm excitation. Emission spectra include sharp lines of 4f-4f transitions of Sm^{3+} ions. All observed bands can be assigned to transitions from excited $^4\text{G}_{5/2}$ to lower $^6\text{H}_J$ levels: $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (565 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (603 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (646 nm), and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ (705 and 715 nm).

Figure 6. (a) Excitation spectra of $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% nanoparticles measured at different temperatures ($\lambda_{\text{em}} = 646 \text{ nm}$); emission spectra of $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% nanoparticles measured at different temperatures upon (b) $\lambda_{\text{ex}} = 350 \text{ nm}$ and (c) $\lambda_{\text{ex}} = 407 \text{ nm}$.

$\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% NPs provided luminescence thermal sensing via ratiometric technique as well as spectral line position and bandwidth. Integral intensities of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transitions upon 350 and 407 nm excitation were calculated to obtain LIRs. Temperature dependence of LIR^{646} for $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% is presented in Figure 7a, whereas Figure S5 and

Figure S6 display evolution of LIR^{565} and LIR^{603} , respectively. To fit experimental dependences, Eq. 1 was used. It was found that an effective gap ΔE was the same irrespective to monitored transition: $1924 \pm 140 \text{ cm}^{-1}$ (646 nm), $1967 \pm 130 \text{ cm}^{-1}$ (565 nm), and $1937 \pm 130 \text{ cm}^{-1}$ (603 nm). Spectral line position and FWHM of $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% charge transfer band as a function of temperature are shown in Figure 7b and Figure 7c, respectively. Both experimental dependences were fitted by linear function.

Figure 7. Evolution of (a) LIR^{646} , (b) spectral line position and (c) FWHM as a function of temperature for $\text{YVO}_4:\text{Sm}^{3+}$ 1 at.% nanoparticles.

3.5 Thermometric performances of Ln^{3+} -doped YVO_4 NPs

To describe the performance of thermometer quantitatively irrespective to their nature and sensing parameter, relative thermal sensitivity was introduced. Relative thermal sensitivity was calculated according to following formula:

$$S_r = \frac{1}{\Lambda} \frac{\partial \Lambda}{\partial T} \cdot 100\% \quad (2)$$

where Λ is the temperature dependent parameter (LIR, spectral line position or FWHM). The calculated relative thermal sensitivities of $\text{YVO}_4:\text{Ln}^{3+}$ ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Sm}^{3+}$) and other Ln^{3+} -doped nanophosphors utilizing different luminescence sensing parameters are summarized in Table 1. As S_r value is temperature dependent, presented values in Table 1 were obtained at the same temperature ($T = 298 \text{ K}$). One can see that LIR sensitivities of $\text{YVO}_4:\text{Ln}^{3+}$ 1 at.% thermometers demonstrate highest values; moreover, S_r increases in $\text{Eu}^{3+}-\text{Dy}^{3+}-\text{Sm}^{3+}$ row. Comparison of LIR sensitivities calculated from different transitions was performed in Table S1. The relative thermal sensitivities for spectral line position and FWHM are situated in the middle and low ranges, respectively, showing values about 0.3 and 0.16 % K^{-1} independently on doping ion.

Second parameter, which is of great importance for thermometers, is the temperature resolution (ΔT)³⁵. This parameter defines how accurate can be thermal sensing using particular thermometer. It was reported earlier that temperature resolution can be obtained using different methods³⁴. Here, ΔT was determined from calibration curve ($\Delta T_{\text{calibr}} = \frac{1}{S_r} \frac{\delta \text{LIR}}{\text{LIR}}$, where $\frac{\delta \text{LIR}}{\text{LIR}}$ is the relative uncertainty in the determination of luminescence intensity ratio obtained from three measurements). The calculated values are presented in Table 1. Noteworthy, all sensing parameters provide sub-degree thermal resolution. As spectral shift and broadening of charge transfer band is more noticeable compared with Ln^{3+} emission peaks, temperature sensing demonstrated in this paper has better resolution.

Table 1. The relative thermal sensitivity (S_r) and temperature resolution (ΔT) of Ln^{3+} -doped luminescence thermometers based on different sensing approaches.

Material	S _r (% K ⁻¹)			ΔT (K)			Ref.
	LIR	Line position	FWHM	LIR	Line position	FWHM	
YVO ₄ :Eu ³⁺ 1 at. %	2.23	0.33	0.16	0.2	0.1	1.5	This work
YVO ₄ :Dy ³⁺ 1 at. %	2.36	0.31	0.15	0.1	0.1	3.0	
YVO ₄ :Sm ³⁺ 1 at. %	3.09	0.33	0.17	0.2	0.1	0.2	
Y ₂ O ₃ :Nd ³⁺ 0.05 at. %	1.51	0.34	0.43	1.1	0.6	0.2	9
Y ₂ O ₃ :Nd ³⁺ 1 at. %	1.37	0.37	0.36	1.0	1.0	0.2	9
Y ₂ O ₃ :Nd ³⁺ 2 at. %	1.51	0.38	0.35	1.3	0.8	0.2	9
YVO ₄ :Nd ³⁺ 0.6 at. %	1.50	0.41	0.07	–	–	–	29,36
YVO ₄ :Nd ³⁺ 2.4 at. %	1.50	0.75	0.14	0.1	17	3	29,36
YVO ₄ :Nd ³⁺ 4.8 at. %	1.30	0.33	0.08	–	–	–	29,36
LiLaP ₄ O ₁₂ :Nd ³⁺ 1%	0.31	0.47	0.32	–	–	–	37
LiNdP ₄ O ₁₂	0.003	0.003	0.46	–	–	–	37
YAP:Nd ³⁺	1.83	–	3.3	0.9	–	0.4	38
LaF ₃ :Nd ³⁺	0.1	0.33	–	2	2	–	39
GeO ₂ –PbO–PbF ₂ : Tm ³⁺ , Yb ³⁺	0.33	0.9	–	0.9	15	–	40

4. CONCLUSIONS

Ln³⁺-doped YVO₄ nanoparticles (Ln³⁺ = Eu³⁺, Dy³⁺, Sm³⁺) synthesized via modified Pechini technique were successfully demonstrated as contactless optical thermometers within 299–466 K temperature range. YVO₄:Ln³⁺ nanopowders had pure tetragonal phase and consisted of quite small nanoparticles with average size about 70–80 nm. Temperature-induced red shift of the CTB edge as well as change of ground level population was utilized as temperature dependent parameters. Temperature sensing was provided through monitoring LIR, spectral line position and bandwidth. All considered temperature sensing strategies were compared in terms of relative thermal sensitivity and temperature resolution. Ratiometric S_r values are affected by doping ion, and reached 3.09 % K⁻¹ for YVO₄:Sm³⁺ nanophosphor, whereas S_r values for spectral line position (~0.3 % K⁻¹) and bandwidth (~0.16 % K⁻¹) are independent on doping ion. The studied nanothermometers provided sub-degree temperature resolution irrespective of sensing strategy. The best accuracy of 0.1 °C was achieved for LIR (YVO₄:Dy³⁺) and line position (YVO₄:Eu³⁺, YVO₄:Dy³⁺, YVO₄:Sm³⁺) as temperature dependent parameters. The obtained results indicated that suggested sensing strategies open an avenue toward multimode high-sensitive optical thermometry.

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REFERENCES

- 1 P. Gschwend, F. Starsich, R. C. Keitel and S. Pratsinis, Nd 3+-doped BiVO 4 luminescent nanothermometers of high sensitivity, *Chem. Commun.*, 2019, **55**, 7147–7150.
- 2 C. D. S. Brites, A. Millán and L. D. Carlos, Lanthanides in Luminescent Thermometry,

- Handb. Phys. Chem. Rare Earths*, 2016, **49**, 339–427.
- 3 E. Hemmer, P. Acosta-Mora, J. Méndez-Ramos and S. Fischer, Optical nanoprobe for biomedical applications: shining a light on upconverting and near-infrared emitting nanoparticles for imaging, thermal sensing, and photodynamic therapy, *J. Mater. Chem. B*, 2017, **5**, 4365–4392.
 - 4 M. Quintanilla and L. M. Liz-Marzan, Guiding rules for selecting a nanothermometer, *Nano Today*, 2018, **19**, 126–145.
 - 5 X. Wang, O. S. Wolfbeis and R. J. Meier, Luminescent probes and sensors for temperature, *Chem. Soc. Rev.*, 2013, **42**, 7834–7869.
 - 6 B. del Rosal, E. Ximendes, U. Rocha and D. Jaque, In Vivo Luminescence Nanothermometry: from Materials to Applications, *Adv. Opt. Mater.*, 2017, **5**, 1600508.
 - 7 X. Xu, Z. Wang, P. Lei, Y. Yu, S. Yao, S. Song, X. Liu, Y. Su, L. Dong and J. Feng, α -NaYb (Mn) F₄: Er³⁺/Tm³⁺@ NaYF₄ UCNP as “band-shape” luminescent nanothermometers over a wide temperature range, *ACS Appl. Mater. Interfaces*, 2015, **7**, 20813–20819.
 - 8 D. Jaque and F. Vetrone, Luminescence nanothermometry, *Nanoscale*, 2012, **4**, 4301.
 - 9 I. E. Kolesnikov, A. A. Kalinichev, M. A. Kurochkin, D. V. Mamonova, E. Y. Kolesnikov, E. Lähderanta and M. D. Mikhailov, Bifunctional heater-thermometer Nd³⁺-doped nanoparticles with multiple temperature sensing parameters, *Nanotechnology*, 2019, **30**, 145501.
 - 10 I. E. Kolesnikov, A. A. Kalinichev, M. A. Kurochkin, E. Y. Kolesnikov and E. Lähderanta, Porphyrins as efficient ratiometric and lifetime-based contactless optical thermometers, *Mater. Des.*, 2019, **184**, 108188.
 - 11 M. Runowski, P. Woźny, I. R. Martín, V. Lavín and S. Lis, Praseodymium doped YF₃: Pr³⁺ nanoparticles as optical thermometer based on luminescence intensity ratio (LIR)–Studies in visible and NIR range, *J. Lumin.*, 2019, 116571.
 - 12 O. A. Savchuk, J. J. Carvajal, P. Haro-Gonzalez, M. Aguiló and F. Díaz, Luminescent nanothermometry using short-wavelength infrared light, *J. Alloys Compd.*, 2018, **746**, 710–719.
 - 13 H. Zheng, B. Chen, H. Yu, J. Zhang, J. Sun, X. Li, M. Sun, B. Tian, S. Fu and H. Zhong, Microwave-assisted hydrothermal synthesis and temperature sensing application of Er³⁺/Yb³⁺ doped NaY (WO₄)₂ microstructures, *J. Colloid Interface Sci.*, 2014, **420**, 27–34.
 - 14 S. A. Wade, S. F. Collins and G. W. Baxter, Fluorescence intensity ratio technique for optical fiber point temperature sensing, *J. Appl. Phys.*, 2003, **94**, 4743–4756.
 - 15 L. Li, Y. Zhou, F. Qin, Y. Zheng, H. Zhao and Z. Zhang, Modified calculation method of relative sensitivity for fluorescence intensity ratio thermometry, *Opt. Lett.*, 2017, **42**, 4837–4840.
 - 16 W. Xu, Q. Song, L. Zheng, Z. Zhang and W. Cao, Optical temperature sensing based on the near-infrared emissions from Nd³⁺/Yb³⁺ codoped CaWO₄, *Opt. Lett.*, 2014, **39**, 4635–4638.
 - 17 X. Tian, X. Wei, Y. Chen, C. Duan and M. Yin, Temperature sensor based on ladder-level assisted thermal coupling and thermal-enhanced luminescence in NaYF₄: Nd³⁺, *Opt. Express*, 2014, **22**, 30333–30345.
 - 18 A. Ćirić, S. Stojadinović and M. D. Dramićanin, Luminescence intensity ratio thermometry and Judd-Ofelt analysis of TiO₂: Eu³⁺, *Opt. Mater. (Amst.)*, 2018, **85**, 261–266.
 - 19 E. C. Ximendes, W. Q. Santos, U. Rocha Silva, K. U. Kumar, F. Sanz Rodríguez, N. Fernández, A. da S. Gouveia Neto, D. Bravo, A. Martín Domingo, B. del Rosal, C. D. S. Brites, L. D. Carlos, D. Jaque, C. Jacinto, U. Rocha, U. K. Kagola, F. Sanz-Rodríguez, N. Fernández, A. da S. Gouveia-Neto, D. Bravo, A. M. Domingo and B. del Rosal, Unveiling in vivo subcutaneous thermal dynamics by infrared luminescent nanothermometers, *Nano*

- Lett.*, 2016, **16**, 1695–1703.
- 20 L. Marciniak, A. Bednarkiewicz, J. Drabik, K. Trejgis and W. Strek, Optimization of highly sensitive YAG: Cr ³⁺, Nd ³⁺ nanocrystal-based luminescent thermometer operating in an optical window of biological tissues, *Phys. Chem. Chem. Phys.*, 2017, **19**, 7343–7351.
 - 21 Y. Pan, X. Xie, Q. Huang, C. Gao, Y. Wang, L. Wang, B. Yang, H. Su, L. Huang and W. Huang, Inherently Eu²⁺/Eu³⁺ Codoped Sc₂O₃ Nanoparticles as High-Performance Nanothermometers, *Adv. Mater.*, 2018, **30**, 1705256.
 - 22 Y. Gao, F. Huang, H. Lin, J. Zhou, J. Xu and Y. Wang, A novel optical thermometry strategy based on diverse thermal response from two intervalence charge transfer states, *Adv. Funct. Mater.*, 2016, **26**, 3139–3145.
 - 23 R. Shi, L. Lin, P. Dorenbos and H. Liang, Development of a potential optical thermometric material through photoluminescence of Pr ³⁺ in La₂MgTiO₆, *J. Mater. Chem. C*, 2017, **5**, 10737–10745.
 - 24 J. Cai, L. Zhao, F. Hu, X. Wei, Y. Chen, M. Yin and C.-K. Duan, Temperature sensing using thermal population of low-lying energy levels with (Sm_{0.01}Gd_{0.99})VO₄, *Inorg. Chem.*, 2017, **56**, 4039–4046.
 - 25 S. Zhou, C. Duan and M. Wang, Origin of the temperature-induced redshift of the charge transfer band of GdVO₄, *Opt. Lett.*, 2017, **42**, 4703–4706.
 - 26 S. Zhou, C. Duan and S. Han, A novel strategy for thermometry based on the temperature-induced red shift of the charge transfer band edge, *Dalt. Trans.*, 2018, **47**, 1599–1603.
 - 27 I. E. Kolesnikov, A. V. Povolotskiy, D. V. Tolstikova, A. A. Manshina and M. D. Mikhailov, Luminescence of Y₃Al₅O₁₂:Eu³⁺ nanophosphors in blood and organic media, *J. Phys. D: Appl. Phys.*, 2015, **48**, 075401.
 - 28 E. V. Golyeva, I. E. Kolesnikov, E. Lähderanta, A. V. Kurochkin and M. D. Mikhailov, Effect of synthesis conditions on structural, morphological and luminescence properties of MgAl₂O₄:Eu³⁺ nanopowders, *J. Lumin.*, 2018, **194**, 387–393.
 - 29 A. A. Kalinichev, M. A. Kurochkin, E. V. Golyeva, A. V. Kurochkin, E. Lähderanta, M. D. Mikhailov and I. E. Kolesnikov, Near-infrared emitting YVO₄:Nd³⁺ nanoparticles for high sensitive fluorescence thermometry, *J. Lumin.*, 2018, **195**, 61–66.
 - 30 Y. H. Zhou and J. Lin, Morphology control and luminescence properties of YVO₄:Eu phosphors prepared by spray pyrolysis, *Opt. Mater. (Amst.)*, 2005, **27**, 1426–1432.
 - 31 A. Huignard, V. Buissette, A.-C. Franville, T. Gacoin and J.-P. Boilot, Emission Processes in YVO₄:Eu Nanoparticles, *J. Phys. Chem. B*, 2003, **107**, 6754–6759.
 - 32 I. E. Kolesnikov, D. V. Tolstikova, A. V. Kurochkin, S. A. Pulkin, A. A. Manshina and M. D. Mikhailov, Concentration effect on photoluminescence of Eu³⁺-doped nanocrystalline YVO₄, *J. Lumin.*, 2015, **158**, 469–474.
 - 33 D. O. Sofich, S. G. Dorzhieva, O. D. Chimitova, B. G. Bazarov, Y. L. Tushinova, Z. G. Bazarova and R. Y. Shendrik, Hypersensitive 5 D 0–7 F 2 Transition of Trivalent Europium in Double Molybdates, *Bull. Russ. Acad. Sci. Phys.*, 2019, **83**, 321–323.
 - 34 I. E. Kolesnikov, A. A. Kalinichev, M. A. Kurochkin, D. V. Mamonova, E. Y. Kolesnikov, A. V. Kurochkin, E. Lähderanta and M. D. Mikhailov, New strategy for thermal sensitivity enhancement of Nd ³⁺ -based ratiometric luminescence thermometers, *J. Lumin.*, 2017, **192**, 40–46.
 - 35 P. Cortelletti, C. Facciotti, I. X. Cantarelli, P. Canton, M. Quintanilla, F. Vetrone, A. Speghini and M. Pedroni, Nd ³⁺ activated CaF₂ NPs as colloidal nanothermometers in the biological window, *Opt. Mater. (Amst.)*, 2017, **68**, 29–34.
 - 36 I. E. Kolesnikov, A. A. Kalinichev, M. A. Kurochkin, E. V. Golyeva, E. Y. Kolesnikov, A. V. Kurochkin, E. Lähderanta and M. D. Mikhailov, YVO₄:Nd³⁺ nanophosphors as NIR-to-NIR thermal sensors in wide temperature range, *Sci. Rep.*, 2017, **7**, 18002.
 - 37 Ł. Marciniak, A. Bednarkiewicz, D. Hreniak and W. Strek, The influence of Nd³⁺ concentration and alkali ions on the sensitivity of non-contact temperature measurements

- in $\text{ALaP}_{12}\text{O}_{40}:\text{Nd}^{3+}$ (A = Li, K, Na, Rb) nanocrystalline luminescent thermometers, *J. Mater. Chem. C*, 2016, **4**, 11284–11290.
- 38 M. A. Hernández-Rodríguez, A. D. Lozano-Gorrín, I. R. Martín, U. R. Rodríguez-Mendoza and V. Lavín, Comparison of the sensitivity as optical temperature sensor of nano-perovskite doped with Nd^{3+} ions in the first and second biological windows, *Sensors Actuators B Chem.*, 2018, **255**, 970–976.
- 39 U. Rocha, C. Jacinto da Silva, W. Ferreira Silva, I. Guedes, A. Benayas, L. Martinez Maestro, M. Acosta Elias, E. Bovero, F. C. J. M. van Veggel and J. A. Garcia Sole, Subtissue thermal sensing based on neodymium-doped LaF_3 nanoparticles, *ACS Nano*, 2013, **7**, 1188–1199.
- 40 I. E. Kolesnikov, M. A. Kurochkin, A. A. Kalinichev, E. Y. Kolesnikov and E. Lähderanta, Optical temperature sensing in $\text{Tm}^{3+}/\text{Yb}^{3+}$ -doped $\text{GeO}_2\text{--PbO--PbF}_2$ glass ceramics based on ratiometric and spectral line position approaches, *Sensors Actuators, A Phys.*, 2018, **284**, 251–259.