Influence of the Synthesis Conditions on the Morphology and Thermometric Properties of the Lifetime-Based Luminescent Thermometers in YPO$_4$:Yb$^{3+}$,Nd$^{3+}$ Nanocrystals

Kamila Maciejewska and Lukasz Marciniak*

ABSTRACT: An increase in the accuracy of remote temperature readout using luminescent thermometry is determined, among other things, by the relative sensitivity of the thermometer. Therefore, to increase the sensitivity, intensive work is carried out to optimize the host material composition and select the luminescent ions accordingly. However, the role of nanocrystal morphology in thermometric performance is often neglected. This paper presents a systematic study determining the role of synthesis parameters of the solvothermal method on the morphology of YPO$_4$:Yb$^{3+}$,Nd$^{3+}$ nanocrystals and their effect on the lifetime of Yb$^{3+}$ ion-based luminescent thermometer performance. It was shown that by changing the RE$^{3+}$:(PO$_4$)$^{3−}$ ratio and the concentration of Nd$^{3+}$ ions, the size, shape, and aggregation level of the nanocrystals can be modified changing the thermometric parameters of the luminescent thermometer. The highest relative sensitivity was obtained for the low RE$^{3+}$:(PO$_4$)$^{3−}$ ratio and 1% Nd$^{3+}$ ion concentration.

1. INTRODUCTION

Materials that exhibit emission of electromagnetic radiation under nonthermal stimuli called phosphors are commonly used primarily in the lighting industry.$^{1−4}$ However, in recent years, they have been increasingly used in many, much more demanding applications. One of the most interesting is the exploitation of luminescence for remote sensing of physical or chemical quantities of the medium in which they are located, including luminescence thermometers, manometers, pH meters, etc.$^{5−10}$ Among these techniques, luminescence thermometry is undoubtedly the most strongly developed.$^{11−19}$ It enables remote readout of temperature by analyzing spectroscopic properties of phosphor. Although the ratiometric approach is the most popular noncontact temperature sensing technique described in the literature, the reliability and accuracy of the temperature readout are significantly limited by the fact that the ratio of the intensity of the two bands can be modified by the medium in which the phosphor is located.$^{17,20}$

Therefore, an important alternative to the ratiometric technique is the lifetime-based approach.$^{17,20−24}$ In the case of luminescence kinetics, the absorption of the emitted radiation by the medium does not significantly affect the lifetimes of excited states and thus does not modify the calibration curve of the thermometer. To increase the sensitivity of a thermometer based on luminescence kinetics, physical processes are sought that will significantly affect the thermal dynamics of the emission level depopulation in a predictable way. In the case of lanthanide ions, the main process responsible for the thermal depopulation of the excited level is the multiphonon depopulation process. However, the probability of this process increases when the number of phonons required to energetically bridge the emitting level with the next lower-lying level decreases. Unfortunately, this leads to the reduction of the luminescence intensity. Therefore, recently there has been increasing interest in the exploitation of alternative processes, among which phonon-assisted energy transfer provides very promising results.$^{25−27}$ In this case, a luminescent ion characterized by high luminescence intensity provided by a high energy separation between the excited and the ground levels and a codoped ion with a configuration of energy levels that serve as an energy acceptor are desirable.$^{28}$ An ideal pair of ions fulfilling these requirements is Yb$^{3+}$, Nd$^{3+}$ ions, where the distance between the ground $^2F_{7/2}$ and excited $^2F_{5/2}$ levels of about 10,000 cm$^{-1}$ limits the probability of multiphonon processes and the $^4F_{3/2}$ level of Nd$^{3+}$ ions located...
about 1500 cm\(^{-1}\) above \(^{2}\text{F}_{5/2}\) can be populated after the absorption of one to two host phonons.\(^{29,56}\) The probability of this process strongly depends on the temperature. A luminescent thermometer could be developed on the basis of this finding.\(^{25–27}\) An additional advantage of using this ion pair is the fact that they operate in the near-infrared spectral range, which can be important for many applications, e.g., biomedicine.\(^{31–33}\) To develop thermometers with the desired properties and thermometric parameters, it is important to understand what material parameters and how they affect the thermometric performance of the phosphor. As our previous studies have shown, the chemical composition of the host material significantly affects the thermometric parameters in \(\text{APo}_4:\text{Nd}^{3+},\text{Yb}^{3+}\) (\(\text{A} = \text{Y, Lu, La, Gd}\)).\(^{22}\)

In this work, the effect of the synthesis parameters on the morphology of \(\text{YPO}_4:\text{Nd}^{3+},\text{Yb}^{3+}\) nanocrystals and their consequences on the thermometric parameters of the phosphor are analyzed. For this purpose, the solvothermal synthesis method in a mixture of ethanol and oleic acid was used.\(^{34,35}\) It was observed that with the increase in the molar concentration of \((\text{PO}_4)^{3−}\) ions relative to \(\text{RE}^{3+}\) cations, the cubic nanoparticles (for \((\text{PO}_4)^{3−}:\text{RE}^{3+} = 0.5\)) change their shape to spherical \((\text{PO}_4)^{3−}:\text{RE}^{3+} = 1\). Further decrease in the \((\text{PO}_4)^{3−}\) concentration causes the lowering of the particle size and facilitates their aggregation. On the other hand, with the increasing concentration of \(\text{Nd}^{3+}\) ions, the morphology of nanocrystals also undergoes a significant modification from spherical nanoparticles, with the shape of nanoparticles changing to cubic and then elongating along one axis to form elongated cuboids (Figure 1).

![Figure 1. Schematic representation of the influence of the synthesis condition on the morphology of the \(\text{YPO}_4:\text{Nd}^{3+},\text{Yb}^{3+}\) nanocrystals.](image)

2. EXPERIMENTAL SECTION

Ytterbium(III) oxide \(\text{Yb}_2\text{O}_3\) (99.99%, Alfa Aesar), europium(III) oxide \(\text{Eu}_2\text{O}_3\) (99.99%, Alfa Aesar), neodymium(III) oxide \(\text{Nd}_2\text{O}_3\) (99.9%, Alfa Aesar), yttrium(III) oxide \(\text{Y}_2\text{O}_3\) (99.99%, Alfa Aesar), sodium phosphate \(\text{Na}_3\text{PO}_4\) (98.0%, Alfa Aesar), oleic acid (90%, Sigma Aldrich), sodium hydroxide (99.8%, POCH S.A., Poland), ethanol (96% pure p.a. POCH S.A. Poland), methanol (POCH S.A., Poland), \(n\)-hexane (POCH S.A., Poland), and chloroform (POCH, Poland) were used without further purification.

In a typical synthesis in a 50 mL autoclave, 0.6 g of NaOH was dissolved into 5 mL of deionized water under stirring. The rare-earth (RE) oxides were dissolved in hydrochloric acid to obtain chloride salts. The resulting rare-earth salts were adjusted to neutral pH by recrystallizing three times with distilled water. Then, the rare-earth chlorides (0.2 M) were added. Thereafter, 10 mL of ethanol and 10 mL of oleic acid were added under vigorous stirring. After 1 h, 5 mL of \(\text{NaH}_2\text{PO}_4\) aqueous solution \((x = 0.1, 0.2, 0.5, \text{and } 1 \text{ M})\) and 10 mL of ethanol were added to the autoclave after stirring for another 30 min. Then, the autoclave was sealed and heated at 180 °C for 8 h. The solution was cooled to room temperature and the nanoparticles were washed with hexane/ethanol by centrifugation. The final product was redispersed in 5 mL of chloroform.

2.1. Methods. Powder diffraction data were obtained using a PANalytical X’Pert Pro diffractometer equipped with an Anton Paar TCU 1000 N temperature control unit using Ni-filtered Cu K\(\alpha\) radiation \((V = 40 \text{ kV}, I = 30 \text{ mA})\). Transmission electron microscopy (TEM) images were performed with a Philips CM-20 SuperTwin transmission electron microscope operating at 160 kV. A drop of the suspension was put on a copper microscope grid covered with carbon. Before the measurement, the sample was dried and purified in an \(\text{H}_2/\text{O}_2\) plasma cleaner for 1 min. The hydrodynamic size of nanoparticles was determined by dynamic light scattering (DLS) using Malvern ZetaSizer at room temperature in a quartz cuvette using hexane as a dispersant. Measurements were made using histograms representing the number of particles per their average size. The emission spectra and luminescence decay profiles were measured using an FLS1000 fluorescence spectrometer from Edinburgh Instruments equipped with a 450 W Xenon lamp and 808 nm line laser as excitation sources and an R928P side window photomultiplier tube from Hamamatsu as a detector. The temperature of the sample was controlled using a THMS 600 heating–cooling stage from Linkam.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Characterization. Depending on the synthesis condition, the \(\text{YPO}_4\) crystallizes in the tetragonal or hexagonal structures.\(^{36–38}\) However, a tetragonal structure is usually observed when higher annealing temperatures are applied, whereas in the case of the as-prepared nanocrystals, a typical hexagonal structure of the \(P_6_{2}2_2\) space group can be found (Figure 2a). In this host material, the \(\text{Y}^{3+}\) ions are coordinated by eight \(\text{O}^{2−}\) ions, and this dodecahedral site can be successfully substituted by lanthanide dopant ions (Figure 2b).\(^{36–38}\) Despite many factors such as \(\text{pH}\), reaction time, and solvent volume ratio, the \((\text{PO}_4)^{3−}:\text{RE}^{3+}\) ratio can most significantly influence the nanocrystal growth process. Therefore, the first aspect in the optimization of the synthesis conditions of \(\text{YPO}_4:\text{Nd}^{3+},\text{Yb}^{3+}\) nanocrystals is to find a proper ratio between phosphate ions \((\text{PO}_4)^{3−}\) and rare-earth ions (RE). It is found that even for the nonstoichiometric ratio between ions, pure phased nanocrystals can be obtained (Figure 2c). However, the comparison of the X-ray diffraction (XRD) patterns of the nanocrystals synthesized using different ionic ratios does not reveal any phase impurities. One can observe that for samples with different \(\text{Nd}^{3+}\) concentrations exhibit a slight shift in the reflections toward lower 2\(\theta\) angles (e.g., from 20.48 to 20.17° for the most intense reflection). This is due to the expansion of the crystallographic cell unit associated with the ion difference between \(\text{Nd}^{3+}\) and \(\text{Y}^{3+}\) ions, which may also be
associated with the preferred orientation of the particles or the preferred growth direction of the nanoparticles. The average particle size determined using the DLS technique indicates that when the \((\text{PO}_4^3^-)\text{:RE}^{3+}\) ratio is below 1, the nanoparticles of average size around 26 nm are obtained (Figure 2d). When the stoichiometric amount of \((\text{PO}_4^3^-)\) ions is applied, an increase
in the particle size to 107 nm is found. A further decrease in the molar amount of the phosphate ions results in an increase in size to 250 nm and 270 nm for the ratios 2 and 5, respectively. However, as is well known, the results obtained from the DLS technique for nonspherical and highly aggregated particles can be misleading. This is particularly important when a PDI close to 1 is obtained. However, in the case of the examined materials with nonaggregated particle form, the PDI values range from 0.002 to 0.310; therefore, the quality of the measurements is satisfactory. The analysis of the TEM images (Figure S1) reveals that for a low (PO4)3−:RE3+ ratio of 0.5, the cubic nanoparticles can be obtained. An increase in the stoichiometric ratio causes the crystallization of relatively large spherical particles. Further increase in the (PO4)3−:RE3+ ratio reduces the size of the particles and facilitates their aggregation. Since the small particle size and nonaggregation are optimized for (PO4)3−:RE3+ = 0.5, this molar ratio is applied in further syntheses. In the second step of the analysis, the influence of the Nd3+ concentration on the structural and morphological properties of the YPO4:2Nd3+,Yb3+ nanocrystals is investigated. It is found that even for 75% Nd3+, the hexagonal structure remains (Figure 2e). However, the morphology differs significantly when the Nd3+ concentration is increased. In the case of as low as 1% Nd3+, the spherical particles are achieved with a diameter of around 14 nm, and an increase in Nd3+ to 25% results in the enlargement of their size to around 60 nm. Surprisingly, a further increase in the Nd3+ concentration enables us to achieve a cube with a size of 40 nm (50% Nd3+) and even rodlike particles with a length of 120 nm and a width of 15 nm (75% Nd3+). As can be clearly seen, the results obtained using the DLS technique are not reliable in this case (Figure 2f).

The luminescent properties of the Nd3+ and Yb3+ ions are very well known. Therefore, only a brief description is given here. Upon 808 nm excitation, the excited state 4F9/2 of the Nd3+ ion can be populated, followed by the fast nonradiative processes causing the population of the emitting 4F7/2 state of the Nd3+. Radiative depopulation of the 4F9/2 state leads to the occurrence of the three emission bands at around 880, 1060, and 1350 nm that can be assigned to the 4F9/2 → 4I9/2, 4F9/2 → 4I11/2, and 4F9/2 → 4I13/2 transitions, respectively. In the presence of the Yb3+ codopant, the 4F9/2 state of the Nd3+ ions can be also depopulated by the energy transfer with the emission of the phonon to the 2F7/2 state of the Yb3+ ions. The high energy separation between the 2F7/2 state and the 2F5/2 ground state (around 10,000 cm−1) prevents efficient depopulation of the excited state of Yb3+ by multiphonon relaxation. However, an increase in temperature results in the growing probability of the back energy transfer to the Nd3+ with the absorption of phonons, thus shortening its lifetime. This preserves high thermal variability of the lifetime of the Yb3+ ions and thus is beneficial from the thermometric perspective. However, in the case of the nanocrystals also, the surface effect significantly affects the luminescent properties of the dopant ions. In the case of the small particles, the energy diffusion among excited states of Yb3+ ions to the surface defects becomes a very efficient channel for the quenching of the luminescence. Thus, the smaller the particle, the shorter the lifetime that is expected in this case. As can be seen, the applied different RE3+: (PO4)3− ratios affect the morphology of the YPO4:10% Yb3+, 50% Nd3+ significantly (Figure 3a−d). Hence, changes in the spectroscopic properties of these particles are expected. The comparison of the low-temperature emission spectra of the YPO4:10% Yb3+, 50% Nd3+ reveals that some changes can be found in the shape of the 4F9/2 → 4I9/2 emission band when the RE3+: (PO4)3− ratio is changed (Figure 3e). The smaller the particle size, the higher intensity of R1 → Z1 and R2 → Z1 electronic transitions between particular Stark components of excited and ground states. This effect can be explained in terms of the energy reabsorption between Nd3+ ions. When the concentration of Nd3+ is high, the light emitted by one of the ions can be absorbed by the other before being emitted from the nanoparticle. The probability of energy reabsorption is the highest for the resonant lines since the population of the Z1 Stark sublevel of the 4I9/2 state is the highest. The larger the size of the particle, the higher the probability of this process because the longer distance photon needs to travel before it leaves the nanoparticle. Therefore, for smaller nanoparticles, more intense R1 → Z1 and R2 → Z1 emission lines can be found by comparing larger counterparts.

Also, the emission intensity ratio of Nd3+ to Yb3+ ions is modified by the size of the particles (Figure 3f). The reduction of the particle size leads to a monotonic increase in the Nd3+ to Yb3+ ratio. This effect can be caused by either the reduction of the Yb3+ emission intensity or a growing emission intensity of Nd3+. Since the spectral position of the emission bands is independent of the RE3+: (PO4)3− ratio, the energy-level configuration of Yb3+ and Nd3+ remains unchanged. Hence, the probability of the interionic energy transfer is expected to be independent of the particle size in this case. Therefore, the observed phenomenon can be explained in terms of two effects. First of them is the light-induced heating of the particles and associated with this more promoted transfer of the electrons from Yb3+ to Nd3+. The efficiency of heat dissipation in strongly dimensionally constrained objects like nanoparticles is strongly limited. Hence, light-induced heating is more efficient for smaller objects. On the other hand, the reduction of the particle size causes an enhancement of the probability of the quenching of the excited state of Yb3+ ions via surface-related quenching processes. Undoubtedly, the change in Yb3+ emission intensity affects the ratio of luminescence intensity of Nd3+ to Yb3+ ions, which is confirmed by the analysis of luminescence kinetics of Yb3+ ions (Figure 3g). It is clearly seen that with the increasing RE3+: (PO4)3− concentration, the average lifetime (τavr, eqs S1 and S2) of the 2F7/2 level is monotonically shortened from τavr = 250 μs for RE = 0.5 to τavr = 48 μs for RE = 5.

To verify the influence of the particle size on the luminescence thermometer parameters based on the lifetime of the 2F7/2 level of Yb3+ ions, the luminescence kinetics was measured as a function of temperature and the average lifetimes were determined (Figures S2 and 4a). As shown in the presented analysis for RE3+: (PO4)3− = 0.5, τavr shortens significantly above 200 K up to about 350 K, above which the rate of observed changes slows down. An increase in the RE3+: (PO4)3− ratio, as shown earlier, reduces the value of τavr and an increase in temperature causes an additional shortening of its value but at a much lower rate than is the case for larger nanoparticles. This effect can be explained by the increased role of surface processes. As it is well known, in the case of materials doped with Yb3+ ions, the energy diffusion across excited 4F9/2 states is very efficient.

For nanomaterials, such a process due to the relatively short ion−surface distance very often leads to energy quenching at the nanocrystal surface through interactions with ligands and functional groups on the
The energy diffusion is a resonant process and its probability should not depend on the temperature, so it effectively shortens the lifetime of $\text{Yb}^{3+}$ ions when it becomes more efficient by reducing the nanoparticle. From a thermometric perspective, this process can be seen as competing with the energy transfer process between $\text{Yb}^{3+}$ and $\text{Nd}^{3+}$; whereas the latter favors increasing the sensitivity of the thermometer, the former suppresses the thermal dynamics of the lifetime changes. For small nanoparticles, it is so efficient that further temperature-induced shortening of $\tau_{\text{avr}}$ values is less evident. The rate of temperature-induced shortening of the $\text{Yb}^{3+}$ ion lifetime can be quantified by the absolute sensitivity ($S_A$) of the luminescence thermometer determined by the following formula:

$$S_A = \frac{\Delta \tau_{\text{avr}}}{\Delta T}$$

where $\Delta \tau_{\text{avr}}$ represents the change in $\tau_{\text{avr}}$ corresponding to the change in temperature by $\Delta T$. As expected, the highest $S_A$ values were obtained for the largest nanoparticles because the longest $\tau_{\text{avr}}$ values were found for these nanoparticles. The maximum value of $S_A = 1.36 \mu s/K$ was obtained at 275 K. Decreasing the size of nanoparticles resulted in a successive decrease in the $S_A$ value. For the smallest nanoparticles ($\text{RE}^{3+}:\text{(PO}_4^{3-})_3$ ratio = 5), the maximum $S_A = 0.06 \mu s/K$ at 220 K. For a further quantitative comparative analysis, the relative sensitivity was also determined according to the equation:

$$S_R = \frac{1}{\tau_{\text{avr}}} \frac{\Delta \tau_{\text{avr}}}{\Delta T} \times 100\%$$

In this case, the highest value of $S_R = 0.9%/K$ was obtained at 300 K for $\text{YPO}_4:10\% \text{Yb}^{3+},50\% \text{Nd}^{3+}$ synthesized using $\text{RE}^{3+}:\text{(PO}_4^{3-})_3 = 0.5$ (Figure 5c). It was worth noting that the temperature at which the maximum sensitivity was obtained for individual samples depended on the size of the nanoparticles and a general trend could be observed that it decreased with the reduction of the size of the luminescent thermometer. The maximum values of $S_R$ decreased monotonically with the $\text{RE}^{3+}:\text{(PO}_4^{3-})_3$ (Figure 5d). The analysis carried out allowed us to conclude that to increase the sensitivity of the luminescence thermometer based on luminescence lifetimes, it was advantageous to use nanoparticles of a larger size. It should be noted here that the hexagonal structure of the $\text{YPO}_4$ was stabilized by the crystallographic OH groups that could affect the population of the excited state of the $2\text{F}_5/2$ state of $\text{Yb}^{3+}$ ions. Hence, the removal of the OH groups at higher temperatures may influence the $\tau_{\text{avr}}$. However, according to the TG-DSC analysis shown by Li et al. in the hexagonal $\text{YPO}_4$, this removal was observed around 470 K. This temperature exceeded the analyzed temperature range in this study.

As indicated by the above studies, the nanocrystal morphology had a significant effect on the thermometric

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**Figure 4.** (a) Thermal dependence of the $\tau_{\text{avr}}$ of $\text{Yb}^{3+}$ ions obtained for different $\text{RE}^{3+}:\text{(PO}_4^{3-})_3$ ratios. The corresponding $S_A$ (b) and $S_R$ (c). (d) Influence of the $\text{RE}^{3+}:\text{(PO}_4^{3-})$ on the maximal $S_R$ (d).

**Figure 5.** Representative TEM images for $\text{YPO}_4:10\% \text{Yb}^{3+}, \% \text{Nd}^{3+}$ nanoparticles with different $\text{Nd}^{3+}$ concentrations: 1% $\text{Nd}^{3+}$ (a), 25% $\text{Nd}^{3+}$ (b), 50% $\text{Nd}^{3+}$ (c), and 75% $\text{Nd}^{3+}$ (d). (e) Comparison of the low-temperature emission spectra upon $\lambda_{\text{exc}} = 808$ nm for different $\text{Nd}^{3+}$ concentrations. (f) $\text{Nd}^{3+}$ to $\text{Yb}^{3+}$ emission intensity ratio as a function of $\text{Nd}^{3+}$ concentration. (g) Influence of the $\text{Nd}^{3+}$ on the $\tau_{\text{avr}}$ of the $2\text{F}_5/2$ state of $\text{Yb}^{3+}$ ions.
performance of a luminescent thermometer based on the luminescence decay times from the $^2F_{5/2}$ level. Taking into account that the phonon-assisted energy transfer to the neighboring Nd$^{3+}$ ion was responsible for the thermal lifetime shortening of this level, one could expect that increasing the Nd$^{3+}$ ion concentration would facilitate this energy transfer by shortening the average Nd$^{3+}$–Yb$^{3+}$ distance. Therefore, the thermometric properties of such a thermometer were expected to depend significantly on the concentration of Nd$^{3+}$ ions. On the other hand, it was known that REPO$_4$ phosphates with large RE ionic radii (such as Nd$^{3+}$) preferentially crystalized in the monoclinic structure and revealed an increased tendency to form elongated rodlike structures. Therefore, it was important to verify how the concentration of Nd$^{3+}$ ions affected the morphology and spectroscopic properties of the obtained phosphors. As mentioned above and illustrated by representative TEM images, the increase in the concentration of Nd$^{3+}$ ions significantly modified the morphology of the sample. For a concentration of 1% Nd$^{3+}$, small, spherical, and nonaggregated nanoparticles were observed (Figure 5a). An increase in the Nd$^{3+}$ concentration to 25% enlarged the size of the nanoparticles while maintaining their shape (Figure 5b). However, the increase in the Nd$^{3+}$ ion concentration to 50% caused a slight decrease in the size of the nanoparticles. Additionally, apart from spherical particles, cubic ones could also be observed (Figure 5c). Further increase in the concentration of Nd$^{3+}$ ions resulted in the elongation of the nanoparticles’ shape by their growth along the c-axis (Figure 5d). Importantly, even for such high concentrations of Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2).

As can be seen, regardless of the Nd$^{3+}$ ion concentration, $\tau_{av}$ shortens above 190 K. However, the rate of this shortening clearly depends on the dopant concentration (Figures 6a and 6b). Additionally, apart from spherical particles, cubic ones could also be observed (Figure 5c). Further increase in the concentration of Nd$^{3+}$ ions resulted in the elongation of the nanoparticles’ shape by their growth along the c-axis (Figure 5d). Importantly, even for such high concentrations of Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2).

Figure 6. Thermal dependence of the $\tau_{av}$ of $^2F_{5/2}$ state of Yb$^{3+}$ ions in YPO$_4$:10% Yb$^{3+}$, Nd$^{3+}$ for different concentrations of Nd$^{3+}$ ions (a); $S_5$ (b) and $S_8$ (c); and influence of the Nd$^{3+}$ concentration on the maximal achieved $S_8$ (d).

As can be seen, regardless of the Nd$^{3+}$ ion concentration, $\tau_{av}$ shortens above 190 K. However, the rate of this shortening clearly depends on the dopant concentration (Figures 6a and 6b). Additionally, apart from spherical particles, cubic ones could also be observed (Figure 5c). Further increase in the concentration of Nd$^{3+}$ ions resulted in the elongation of the nanoparticles’ shape by their growth along the c-axis (Figure 5d). Importantly, even for such high concentrations of Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2). A comparison of the luminescence spectra of YPO$_4$:Nd$^{3+}$ ions, the hexagonal structure was maintained (Figure 2).

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**4. CONCLUSIONS**

The solvothermal synthesis parameters of YPO$_4$:Nd$^{3+}$,Yb$^{3+}$ nanocrystals significantly affect the morphology of the final product. It has been shown that using low RE$^{3+}$/(PO$_4$)$^{3-}$ concentrations can deliver cubic and well-separated nanocrystals while increasing the RE$^{3+}$/(PO$_4$)$^{3-}$ ratio results in a decrease in the size of nanoparticles, changing their shape to spherical and increasing the degree of aggregation. This significantly affects not only the spectroscopic properties of YPO$_4$:Yb$^{3+}$,Nd$^{3+}$ but also the thermometric performance of the thermometer based on the luminescence kinetics of the $^2F_{5/2}$ level of Yb$^{3+}$ ions. The decrease in nanoparticle size increases the role of surface quenching processes in the luminescence of Yb$^{3+}$ ions manifested in the shortening of the lifetime of the $^2F_{5/2}$ level and decrease in the emission intensity of the $^2F_{5/2} \rightarrow$
2F_{5/2} \text{ band with respect to the } 4F_{5/2} \rightarrow 4I_{9/2} \text{ band of Nd}^{3+} \text{ ions. The surface luminescence quenching processes competing with the energy transfer process involving Yb}^{3+} \rightarrow \text{Nd}^{3+} \text{ phonons decrease the absolute and relative sensitivity of the luminescence thermometer. An increase in the concentration of Nd}^{3+} \text{ ions changes the shape of nanoparticles from spherical to cubic (50% Nd}^{3+} \text{) or even rodlike (75% Nd}^{3+} \text{). Cross-relaxation-activated processes decrease the luminescence intensity of the Nd}^{3+} \text{ band relative to the Yb}^{3+} \text{ band with the increasing Nd}^{3+} \text{ concentration. Interestingly, the shape of the luminescence spectra recorded for Nd}^{3+} \text{ concentrations above 50% suggests that a monoclinic structural phase is present in the samples despite the fact that the XRD falls indicate the presence of only hexagonal structure. Considering the linear decrease in the maximum relative sensitivity of the luminescent thermometer with increasing Nd}^{3+} \text{ ion concentration, it can be concluded that the concentration of Nd}^{3+} \text{ ions has a dominant influence on the thermometric parameters of this type of thermometer. The presented studies indicate the important role of nanocrystal morphology on thermometric performance, which is often not considered, or not analyzed.}

## ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03990.

Additional TEM images and luminescence decay profiles measured at different temperatures (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Łukasz Marciniak — Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-422 Wroclaw, Poland; orcid.org/0000-0001-5181-5865; Email: l.marciniak@intibs.pl

### Author

Kamila Maciejewska — Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-422 Wroclaw, Poland; orcid.org/0000-0002-8411-3234

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.2c03990

Notes

The authors declare no competing financial interest.

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