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Supporting Informations

Size dependent sensitivity of Yb^{3+},Er^{3+} up-converting luminescent nano-thermometers

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XRD patterns of fluorides and tetraphosphates of different nanoparticles' size are presented in Fig. S1. was Powder X-ray diffraction (XRD) reflection peaks of β-$NaYF_4$ nanocrystals doped with lanthanide ions are in agreement with the standard pattern JCPDS card # 41-5868 indicating pure hexagonal phase of nanocrystals (Fig. S1a). The variation in the intensity of XRD peaks for the nanocrystals may be interpreted due to the crystallite size and morphology variations. [1] Additionally, a change in the orientation of the nanocrystals along a preferred direction may interfere in the intensity along the most favorable direction. The peak shifting confirms the perturbation in the crystal lattice caused by replacement of Y^{3+} by smaller radius Lu^{3+}. [2]. Analogously XRD patterns obtained for $LiLaP_4O_{12}$:Er^{3+},Yb^{3+} nanocrystals are presented in Fig. S1b. As it can be noticed all of observed diffraction peaks correspond to the reference pattern for monoclinic structure of $LiLaP_4O_{12}$ (ICSD 33241).

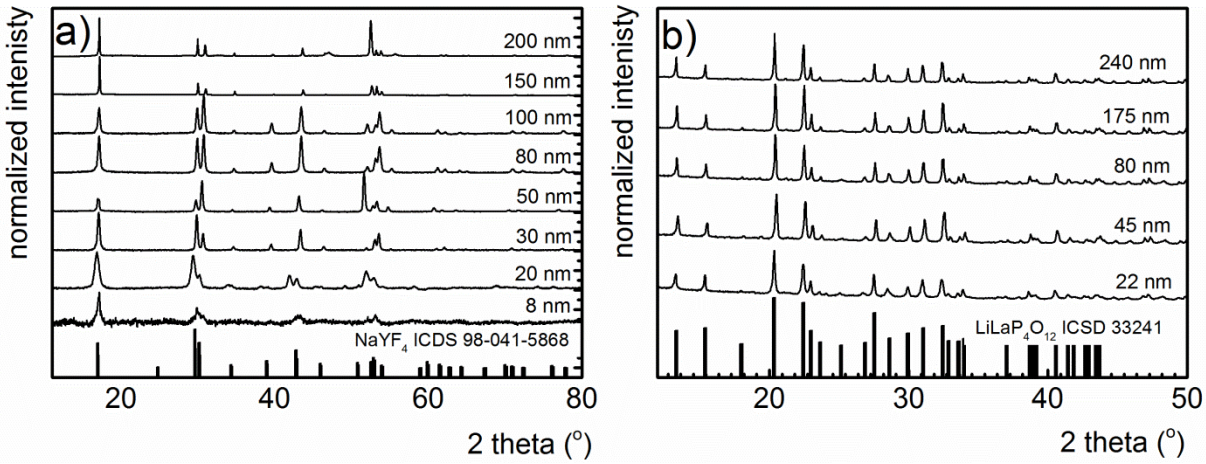

Figure S1. XRD patterns of $NaYF_4$:Yb^{3+},Er^{3+} – a and $LiLaP_4O_{12}$: Yb^{3+},Er^{3+}-b nanocrystals.

Table 1. Synthesis conditions for $NaYF_4$ and $LiLaP_4O_{12}:Er^{3+},Yb^{3+}$ nanocrystals

Size [nm]	Composition	Structure	Method of synthesis	Synthesis parameters				
				Reactants	Solvents	Time [min]	Temp [˚C]	Annealing temperature
8	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}	hexagonal	Thermal decoposition	0.75 mmol $Ln(COO)_3$, 18 mmol NH_4F, 13 mmol NaOH	20 ml oleic acid + 20 ml octadecene	30	300	-
20	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}	hexagonal	Thermal decomposition					-
30	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}, 2% Lu^{3+}	hexagonal	Thermal decomposition					-
50	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}, 5% Lu^{3+}	hexagonal	Thermal decomposition	2.5 mmol $Ln(COO)_3$ 10 mmol NH_4F, 6.25 mmol NaOH	15 ml oleic acid + 38 ml octadecene	60	300	-
80	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}, 10% Lu^{3+}	hexagonal	Thermal decomposition					-
100	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}, 20% Lu^{3+}	hexagonal	Thermal decomposition					-
150	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}, 30% Lu^{3+}	hexagonal	Thermal decomposition					-
200	$NaYF_4$: 2% Er^{3+}, 20% Yb^{3+}, 50% Lu^{3+}	hexagonal	Thermal decomposition					-
22	$LiLaP_4O_{12}$: 5% Er^{3+},50% Yb^{3+}	monoclinic	Co-precipitation	Li_2CO_3, La_2O_3, Yb_2O_3, Er_2O_3 $(NH_4)_2HPO_4$	water	-	-	450
45	$LiLaP_4O_{12}$: 5% Er^{3+},50% Yb^{3+}	monoclinic	Co-precipitation			-	-	500
80	$LiLaP_4O_{12}$: 5% Er^{3+},50% Yb^{3+}	monoclinic	Co-precipitation			-	-	600
170	$LiLaP_4O_{12}$: 5% Er^{3+},50% Yb^{3+}	monoclinic	Co-precipitation			-	-	700
240	$LiLaP_4O_{12}$: 5% Er^{3+},50% Yb^{3+}	monoclinic	Co-precipitation			-	-	800

Representative up-conversion emission spectra of $NaYF_4:Yb^{3+},Er^{3+}$ and $LiLaP_4O_{12}:Yb^{3+},Er^{3+}$-b measured at different temperatures are presented in Fig. S2 a and b and respectively. In both of these cases emission spectra consist of three emission bands localized at 520 nm, 550 nm and 650 nm corresponding to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ respectively.

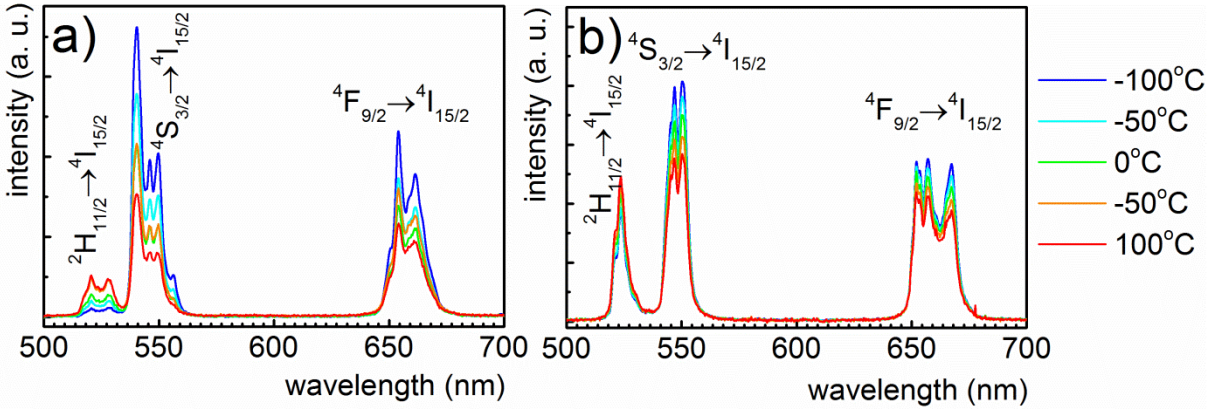

Figure S2 Representative emission spectra $LiLaP_4O_{12}$: Yb^{3+},Er^{3+}-a; and $NaYF_4$:Yb^{3+},Er^{3+} – b.

A room temperature luminescence decay profiles of $^4S_{3/2}$ –a and $^2H_{11/2}$ –b states of Er^{3+} ions in $NaYF_4$:Yb^{3+},Er^{3+} nanocrystals as a function of nanoparticles' size upon 980 nm excitation line are presented in Fig. S3.

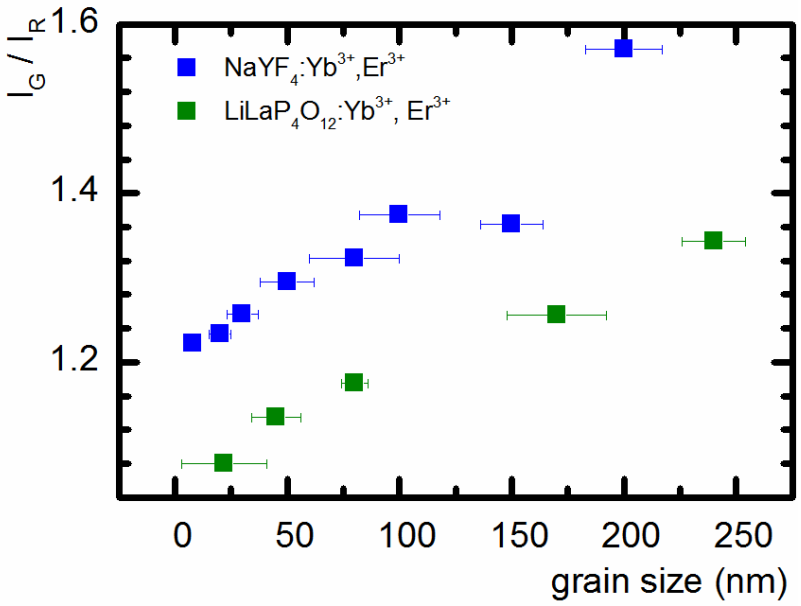

Figure S3. The influence of nanoparticles' size on Green to Red emission intensity ratio fro $NaYF_4$:Yb^{3+},Er^{3+} and $LiLaP_4O_{12}$:Yb^{3+},Er^{3+} nanocrystals measured at 30 °C.

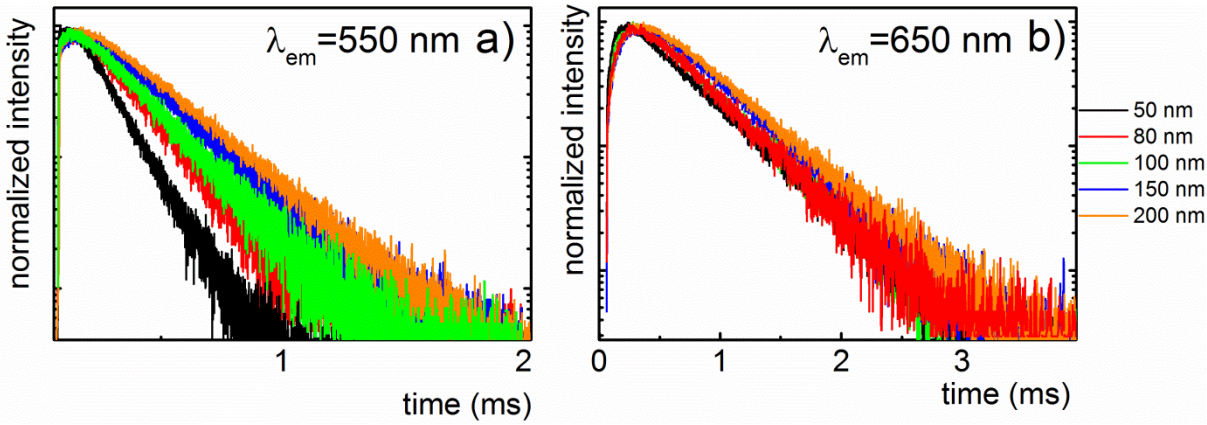

Figure S4. Room temperature luminescence decay profile of $NaYF_4:Yb^{3+},Er^{3+}$ nanocrystals of $^4S_{3/2}$ state (λ_{em}=550 nm) – a; and $^4F_{9/2}$ state (λ_{em}=650 nm) – b.

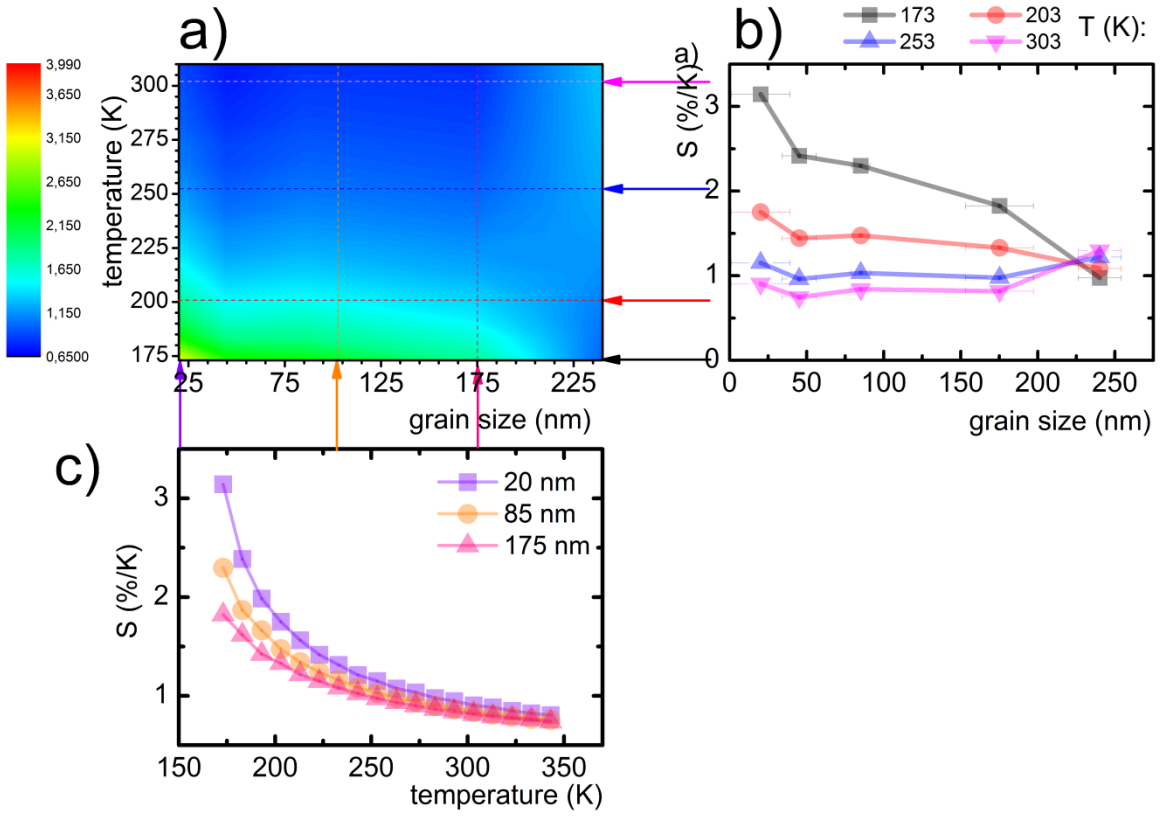

Figure S 5. Color map presents the influence of the nanoparticles' size on the sensitivity of $LiLaP_4O_{12}:Yb^{3+},Er^{3+}$ nanocrystals at different temperatures -a); representative examples of size effect on sensitivity of luminescent thermometers at different temperatures-b, and thermal evolution of sensitivity for different nanoparticles' size -c).

References

[1] M. Inoue, I. Hirasawa, The relationship between crystal morphology and XRD peak intensity on CaSO4·2H2O, Journal of Crystal Growth, 380(2013) 169-75.

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