Supplementary Information

Optimizing the composition of LaF_3:Yb,Tm upconverting nanoparticles synthesised by co-precipitation method to improve the emission intensity

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Synthesis of nanoparticles

Table S1: Amounts of rare earth metal ion solutions used in the synthesis for the different composition of $La_{(1-x-y)}Yb_xTm_yF_3$ nanoparticles.
In case of 100% conversion rate the maximum yield of doped LaF_3 material was 2.00 g.

x	y	1 M La^{3+} solution [ml]	50 mM Yb^{3+} solution [ml]	5 mM Tm^{3+} solution [ml]
1.0	0.1	10.10	2.04	2.04
2.0	0.1	9.99	4.08	2.04
3.0	0.1	9.89	6.13	2.04
4.0	0.1	9.79	8.17	2.04
5.0	0.1	9.69	10.20	2.04
6.0	0.1	9.59	12.26	2.04

TEM-EDS analysis of the nanoparticles

TEM-EDS analysis was carried out on the LaF_3: 1-6 mol% Yb, 0.1 mol% Tm upconverting nanoparticles heat treated at 400 °C. (The EDS elemental maps of the samples were measured, however, the low amounts of ytterbium and thulium present in the samples, and their partially overlapping peaks in the EDS spectra, in addition with the significant carbonization of the samples, caused the elemental maps to be unreliable. Instead of the elemental maps, the composition of the particles was determined using the TEM EDS measurement taken from a larger area of the sample.) An example EDS spectrum can be seen in Figure A1. The spectra showed the highest peaks belonging to La, F, C and O, showing that it was mainly made of LaF_3, and the sample contained some organic pollutants. The low intensity Cu and Mo peaks appearing in the spectra can be attributed to the background due to the sample grid and sample holder. Low intensity peaks also showed the presence of the doping ions, Tm and Yb, although it should be noted that the Tm and Yb peaks partially overlap, making the determination of their exact concentration difficult. Very small Na and Si peaks also appear on the spectra, which might come from pollutants and synthesis by-products that can be present in the sample in small amounts.

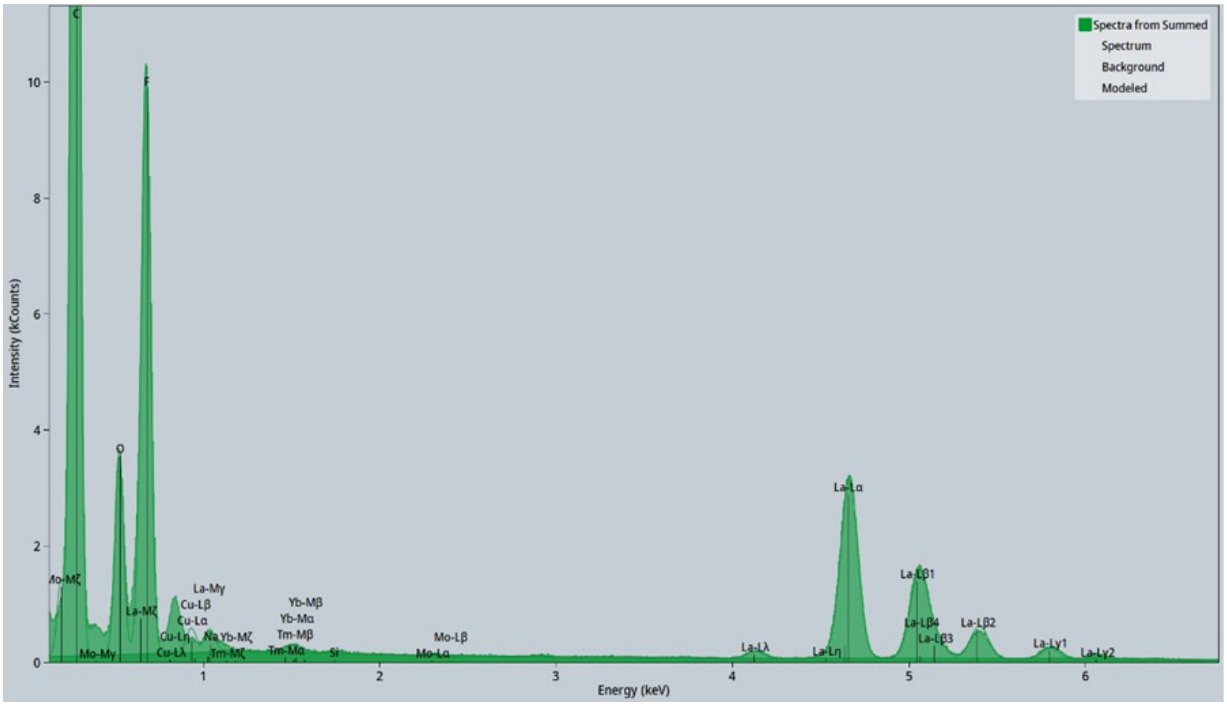

Fig. S1: TEM EDS spectrum of LaF_3: 1 mol% Yb, 0.1 mol% Tm sample heat treated at 400 °C

Upconversion emission measurements

Emission spectra of heat treated samples

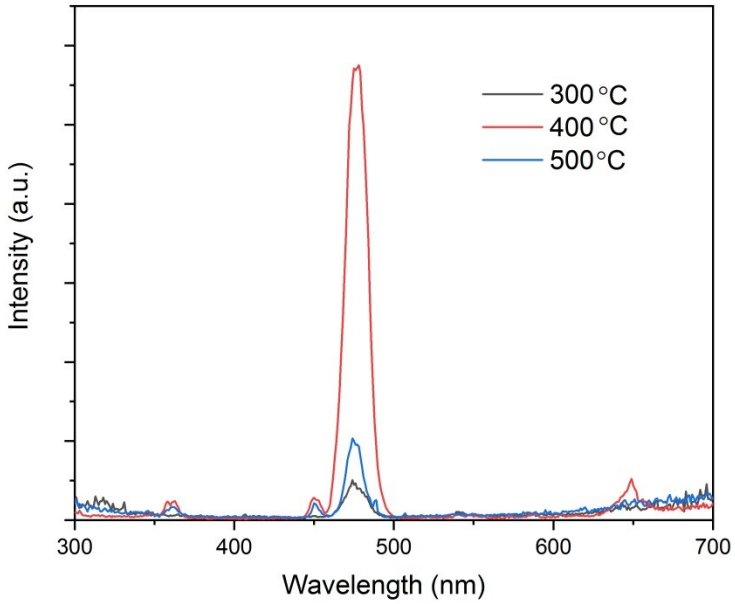

Fig. S2: Upconversion emission spectra of LaF_3: 2 mol% Yb, 0.1 mol% Tm sample heat treated at different temperatures (excitation wavelength: 980 nm; laser power: 1.49 W)

Laser power dependent emission spectra

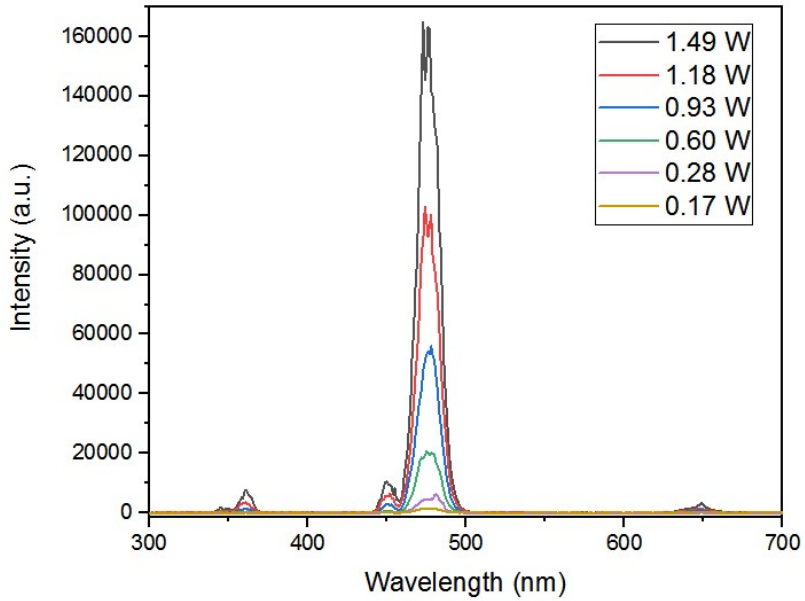

Fig. S3 Laser power dependence of the upconversion emission spectra of LaF_3: 3 mol% Yb, 0.1 mol% Tm sample

XRD measurements on samples before and after heat treatment

Fig S4. shows the XRD patterns of LaF_3: 4% Yb, 0.1% Tm nanoparticles before heat treatment and after heat treatments at different temperatures. The peaks that can be attributed to hexagonal LaF_3 structure (PDF-00-032-0483) appeared in all samples. The XRD pattern of the sample heat treated at 300 °C showed peaks similar in shape and intensity to those of the as-prepared sample, while the samples treated at 400 and 500 °C showed peaks with increasingly higher intensity and a narrower shape, suggesting higher crystallinity. The sample heat treated at 500 °C showed new peaks appearing (noted with an asterisk in Fig S4), which do not belong to the hexagonal LaF_3 structure. Based on the results published our previous paper [*B. Tegze, G. Tolnai, D. Hessz, M. Kubinyi, J. Madarász, G. Sáfrán and Z. Hórvölgyi, J. Therm. Anal. Calorim., 2023, 148, 10795–10802*], it can be assumed that this is caused by crystalline by-products (e.g. YbOF and YbOOH) forming at this higher temperature, which can also contribute to the lowered emission intensity of samples heat treated above 400 C.

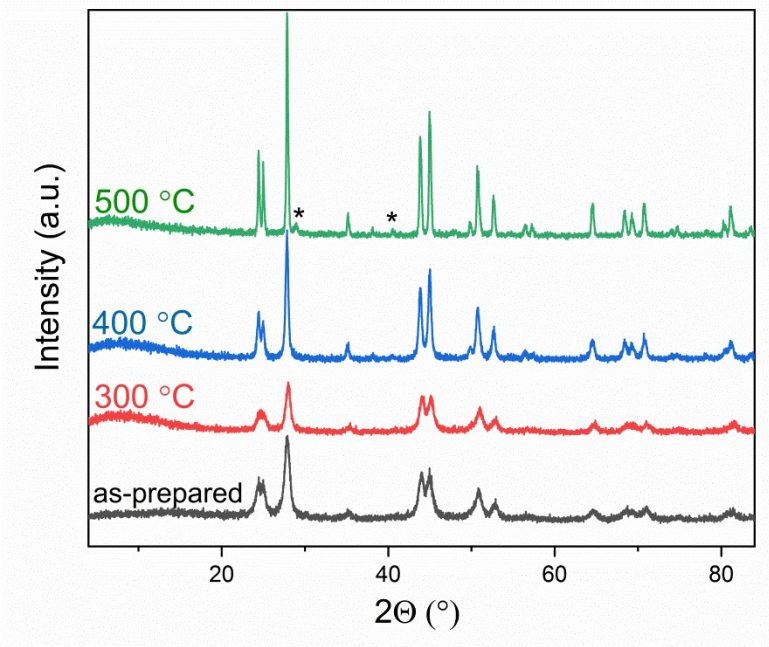

Fig. S4 XRD patterns of the LaF_3: 4% Yb, 0.1% Tm sample before heat treatment (as-prepared), and after heat treatment at different temperatures (300-500 °C, for 2 h in each case)