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ARTICLE TYPE

Band structure, Shape controllable synthesis and Luminescence properties of precursor and final product Lu₆O₅F₈:Eu/Tb/Ce/Dy nano/microstructures

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Fig. S1 shows XRD patterns of the corresponding precursor ¹⁰ prepared under different pH values with different pH regulators calcined at 580 °C for 4 h. It is obvious that the locations and relative intensities of the diffraction peaks coincide well with the data reported in the Ref. [20]. No additional peaks of other phases are found, indicating that the pure-phase Lu₆O₅F₈ is obtained,

¹⁵ except the sample prepared at pH=1, because there are some impure peaks in the range of 25-28 °C.



Fig. S1 XRD patterns of precursor after calcination at 580 °C for 4 h prepared at various pH values: (a) pH =1, 3, 7, 9; (b) pH=11, 13 using NH3•H2O as pH regulator; (c) pH=11, 13 using NaOH as pH regulator

The composition and phase purity of the as-prepared precursor with different additives and the final product after calcination at 580 °C were also examined by XRD, shown in the Fig. S2. It can be seen clearly from Fig. S2a that the phase of the precursor is ²⁵ matched well with Y(OH)_{1.63}F_{1.37} (JCPD Standard Card No. 80-2008) perfectly except for the peak shifting. While after annealing at 580 °C for 4 hours, the product is transformed into pure Lu₆O₅F₈ phase reflected from the XRD pattern in Fig. S2b.



Fig. S2a XRD patterns of samples prepared using different additives in alkaline environment; Fig. S2b XRD patterns of the above samples after calcination at 580 °C for 4h SEM images of samples with different amounts of EDA were shown in Fig. S3. When 1 mL EDA was added into the solution,
the morphology is rods with average diameter of 1 μm and length up to 4.5 μm but not well dispersed (Fig. S3a). A magnified SEM image (Fig. S3b) indicates that the tubes have open ends, while the inner surface of the rods is not very regular. As shown in Fig. S3c, when 3 mL EDA was added into the solution,
monodisperse and regular bundles are observed. From the enlarged image of Fig. S3d, numerous uniform rods with are observed to assemble to the cluster. Upon a further increase of the amount of EDA to 5 mL, the cluster morphology maintained basically except the cluster became slender (Fig. S3e, 3f).



Fig. S3 SEM images of samples with different amounts of EDA: (a, b) 1 mL; (c, d) 3 mL; (e, f) 5 mL.

Enlarged SEM micrograph (Fig. S4) reveals the interesting ⁵⁰ fact that the NH₄LuF₄ flower-like structures are assembled by many interweaving and slightly bending nanoflakes with a thickness of 25 nm.



Fig. S4 Enlarged SEM micrograph of sample prepared with EDTA as chelating agent, NH₃•H₂O as pH regulator

- For the excellent materials for PDP, the abilities to absorb energy 5 strongly in the VUV region and then give a strong visible emission are critical. Fig. S5 presents the emission spectra of $Lu(OH)_{1.57}F_{1.43}/Lu_6O_5F_8:Tb^{3+}/Eu^{3+}$ under excitation at 147 nm. To optimize the activator content doped in the host lattice, we measured the emission intensity as a function of Eu³⁺ 10 concentration relative to Lu³⁺, as shown in Fig. S5a. All the spectra consist of sharp lines ranging from 580 to 720 nm, which are associated with the transitions from the excited ${}^{5}D_{0}$ level to the ${}^{7}F_{I}$ (J = 1-4) levels of the Eu³⁺ activators. The major emissions of the samples are at 594 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$), 619 nm (${}^{5}D_{0}$ $_{15} \rightarrow ^7F_2$), 697 and 703 nm ($^5D_0 \rightarrow ^7F_4$), and the strongest emission peak is at 619 nm. It is obvious that the PL intensities became enhanced as the Eu3+ concentration increased, and the PL intensity was found to decrease for a concentration of doped Eu³⁺ greater than 5%, which is attributed to a concentration-quenching
- $_{20}$ effect. After heat treatment, it could be found from Fig. S5b that the peak profiles are similar to that before heat treatment, but the PL intensity decreased greatly. From Fig. S5c and 5d, one can notice that the 5D_3 emission decreased while the 5D_4 emission of Tb^{3+} increased with an increase in the Tb^{3+} content, which is due
- ²⁵ to the cross relaxation between the ${}^{5}D_{3}$ → ${}^{5}D_{4}$ transition and ${}^{7}F_{6}$ → ${}^{7}F_{0}$ transitions of Tb³⁺. Meanwhile, the ${}^{5}D_{4}$ emission reached a maximum at x = 15% and then decreased, which is caused by concentration quenching effect. The ${}^{5}D_{4}$ emission of Tb³⁺ increased rapidly with an increase in the concentration of Tb³⁺.
- ³⁰ This is due to several factors, including the cross relaxation between the ${}^{5}D_{3}$ and ${}^{5}D_{4}$ levels mentioned above, an increase in the number of luminescence centers, and the quantum cutting, etal.



 $\begin{array}{l} \mbox{35} \quad \mbox{Fig. S5 PL emission spectra of } Lu(OH)_{1.57}F_{1.43}:x\%Eu^{3+} (1 \le x \le 15) (a); \\ Lu_6O_5F_8: x\% Eu^{3+} (1 \le x \le 15) (b); \ Lu(OH)_{1.57}F_{1.43}:x\%Tb^{3+} (1 \le x \le 20) (c); \\ Lu_6O_5F_8: x\% Tb^{3+} (1 \le x \le 20) (d) \ under \ excitation \ at 147nm \end{array}$