

Article

Effects of Rare-Earth Elements Doping on Micro-Structure and Fluorescence Performances of Fluorapatite

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Abstract: For purposes of optimizing the microstructure and fluorescence properties of rare-earth elements (REEs)-doped fluorapatites (FAPs), various kinds of REEs (La, Pr, Sm, Eu, Gd, Ho, Er, and Yb) with the concentration of 2~20 mol.% have been inserted into the FAPs framework via hydrothermal method, in order to investigate the influential mechanism of the REEs on the crystal structure, morphology, and fluorescence under the excitation of the near-ultraviolet light of the FAPs. Experimental results show that the wavelength of the emitted light of the REEs-doped FAPs is decided by the type of REEs. Unlike the Pr/Yb- and Ho-doped FAPs and with the fluorescence of red and green emitted light, respectively, the Er-doped FAPs show a blue light emission with wavelengths of 296, 401, and 505 nm, which is, moreover, different with the Eu-doped FAPs, showing an orange light emission with wavelengths of 490, 594, and 697 nm. The emission luminous color is related to the lattice defects of the FAPs doped with the various types and the effective doping concentration of the REEs. The luminous intensity increases with the increase in the effective doping concentration of the REEs. Nevertheless, the formation of rare-earth fluoride results in the decrease in the effective doping concentration of the REEs and the luminous intensity. The FAPs with an effective doping concentration of 7 mol.% Er and 3 mol.% Eu show relative excellent fluorescence properties.



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Keywords: rare-earth element; fluorapatite; morphology; microstructure; luminescence

1. Introduction

The fluorapatites (FAPs, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), as a kind of biomedical material, are widely used for the manufacturing of orthopedic implants, dental ceramics, and sustained-release carrier, owing to their excellent biocompatibility [1–5]. Nonetheless, the calcium ion with a fully outermost electron orbital mean that pure FAPs cannot emit visible light under ultraviolet excitation, which finally causes it to be not able to be tracked via bioimaging technologies [6,7].

Fortunately, the structural flexibility of the FAPs permits the substitutes diverse rare-earth elements (REEs) ions for calcium ions [8–10]. The active electrons in the 4f sub-shell can be excited to bring about energy level transition, resulting in REEs ions that can absorb and emit light of particular frequencies [11–13]. As a consequence, the REEs-doped FAPs can generate a broad range of absorption and fluorescence spectra spanning from ultraviolet to visible or infrared light under the excitation of the near-ultraviolet light [14–22].

Numerous studies claim that the element types of the REEs play a basic role on the fluorescence properties of the REEs-doped inorganic substance [14–17]. Yang H. et al. [14] has reported that the Nd^{3+} -doped Gd_2O_3 shows excellent luminous performances under the excitation of the near-infrared light with a wavelength of 808 nm. Zhang Z. et al. [15] found that the Sm-doped $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ shows an orange-red emission peak with a wavelength of 600 nm under the excitation of near-ultraviolet light. Baghel S. K et al. [16] demonstrated

that Ce-doped $\text{SrZrSi}_2\text{O}_7$ synthesized via the solid-state reaction method exhibits a broad excitation peak at a wavelength of 293 nm and an emission peak with a wavelength of 480 nm (blue range) [17].

Meanwhile, a great number of researchers have also proven that the luminous intensity and emission light color of the REEs-doped inorganic substance are directly determined by the effective doping concentration of the REEs [18]. Mariappan A. et al. have reported that Eu^{3+} -doped $\text{Ce}_{0.2}\text{Gd}_{0.2}\text{Hf}_{0.2}\text{La}_{0.2}\text{Zr}_{0.2}\text{O}_2$ nanoparticles with increasing Eu^{3+} concentration show various emission colors tuned from orange to red [19]. Hua Y. et al. [20] found that the luminous intensity of Eu-doped $\text{Sr}_2\text{LaNbO}_3$ shows a trend of first increasing and then decreasing with the increase in the effective Eu doping concentration. Senden T. et al. [21] demonstrated that the concentration quenching effects are limited under a concentration of Mn ions lower than 5 mol.% but the quantum efficiency decreases as the concentration is higher than 10 mol.% due to direct energy transfer to quenching sites (defects and impurity ions). Kuamr P. et al. [22] found that an increase in the doping concentration of Sm ions results in the luminous intensity of Sm-doped $\text{Y}_4\text{Al}_2\text{O}_9$ first increasing and then decreasing due to the nonradiative energy transfer. Unfortunately, the effects mechanism of doping REEs and their content on the fluorescence of fluorapatite remain to be understood.

In this paper, La-, Pr-, Sm-, Eu-, Gd-, Ho-, Er-, and Yb-doped FAPs with various effective doping concentrations ranging 1 to 20 mol.% have been synthesized via hydrothermal method. The crystal structure and morphology of the REEs-doped FAPs have been investigated to reveal the effects of the doping element types and the concentration of the REE ions on the luminescence of fluorapatite.

2. Experimental

To form the REEs-doped FAPs, La, Pr, Sm, Eu, Gd, Ho, Er, and Yb ions were doped to replace calcium ions in FAPs. Figure 1 is the flowchart showing the synthesizing of the REEs-doped FAPs. Prior to the hydrothermal synthesis of the REEs-doped FAPs, precursor solution (A) was prepared via mixing 0.1 mol/L $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.03 mol/L cetyltrimethylammonium bromide (CTAB), and various REEs–nitrate and stirring in deionized water. The anionic ligand solution (B) is the mixture solution of 0.267 mol/L $\text{Na}_3\text{Cit} \cdot 2\text{H}_2\text{O}$, 0.267 mol/L NaF, and 0.111 mol/L $(\text{NH}_4)_2\text{HPO}_4$. The prepared anionic ligand and precursor solution were mixed by magnetic stirring. During hydrothermal synthesis, the anionic ligand and precursor solutions were hydrothermally treated under a temperature of 180 °C for 24 h. Precipitation with the REEs-doped FAPs was formed in the mixture solution. After hydrothermal synthesis, the REEs-doped FAPs were collected via the processing of centrifugation (15 min, 8000 r/min), deionized water and ethanol washing, and, finally, drying at 80 °C for 12 h. The effective doping concentration of the REEs was decided by controlling the molar ratio of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and REEs–nitrate. The detailed molar ratio of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and REEs–nitrate in precursor solution for each sample is shown in Table 1. The theoretical doping concentrations of the REEs (La, Pr, Sm, Eu, Gd, Ho, Er, and Yb) in the FAPs are 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 mol.%.

The crystallographic lattice constants and phase structure of the REE-doped FAPs were identified by a Rigaku Smart-Lab SE model X-ray diffraction (XRD) using a $\text{Cu-K}\alpha$ radiation source (wavelength of 1.5406 Å), a 2θ range of 5–120°, and a continuous scan speed of 2°/min. The structure was also refined by utilizing the GSAS II 5438 software which is designed by Argonne National Laboratory, USA, and the lattice constants were also calculated via the Rietveld structural refinement in the GSAS II software. The initial set for refinement was based on the $\text{P6}_3/\text{m}$ space group and its corresponding atomic positions [23]. The background is modeled using a 12th-order polynomial. Then, the data acquired from the XRD experiment were fitted using the Lorentzian and Gaussian functions. The occupancy factors for oxygen, fluorine, and phosphorous were presumed to remain constant, consistent with the stoichiometry of the FAPs.

The particle size, microstructure, and morphology of the REEs–Faps were analyzed by a ThermoFisher Talos F200X model transmission electron microscope (TEM) equipped with energy-dispersive X-ray detector (EDS), which were purchased from Thermo Fisher Scientific Inc., Waltham, MA, USA. The TEM tests of the pure and REEs-doped Faps were conducted under room temperature and an accelerating voltage of 200 KeV. The morphology and element spectrum of the REE–Faps were also observed by Hitachi SU8220 scanning electron microscope (SEM) equipped with the FEI Quanta 200 FEG model EDS, which were purchased from Hitachi, Tokyo, Japan, and Thermo Fisher Scientific Inc., Waltham, MA, USA.

The Edinburgh FS5/Hitachi F4600 model, purchased by Edinburgh Instruments, Livingston, Scotland, UK, fluorescence spectrofluorometer was used to record excitation and emission spectra of the REEs-doped Faps under the excitation light wavelength of 440 nm and the emission light wavelength of 250 nm.

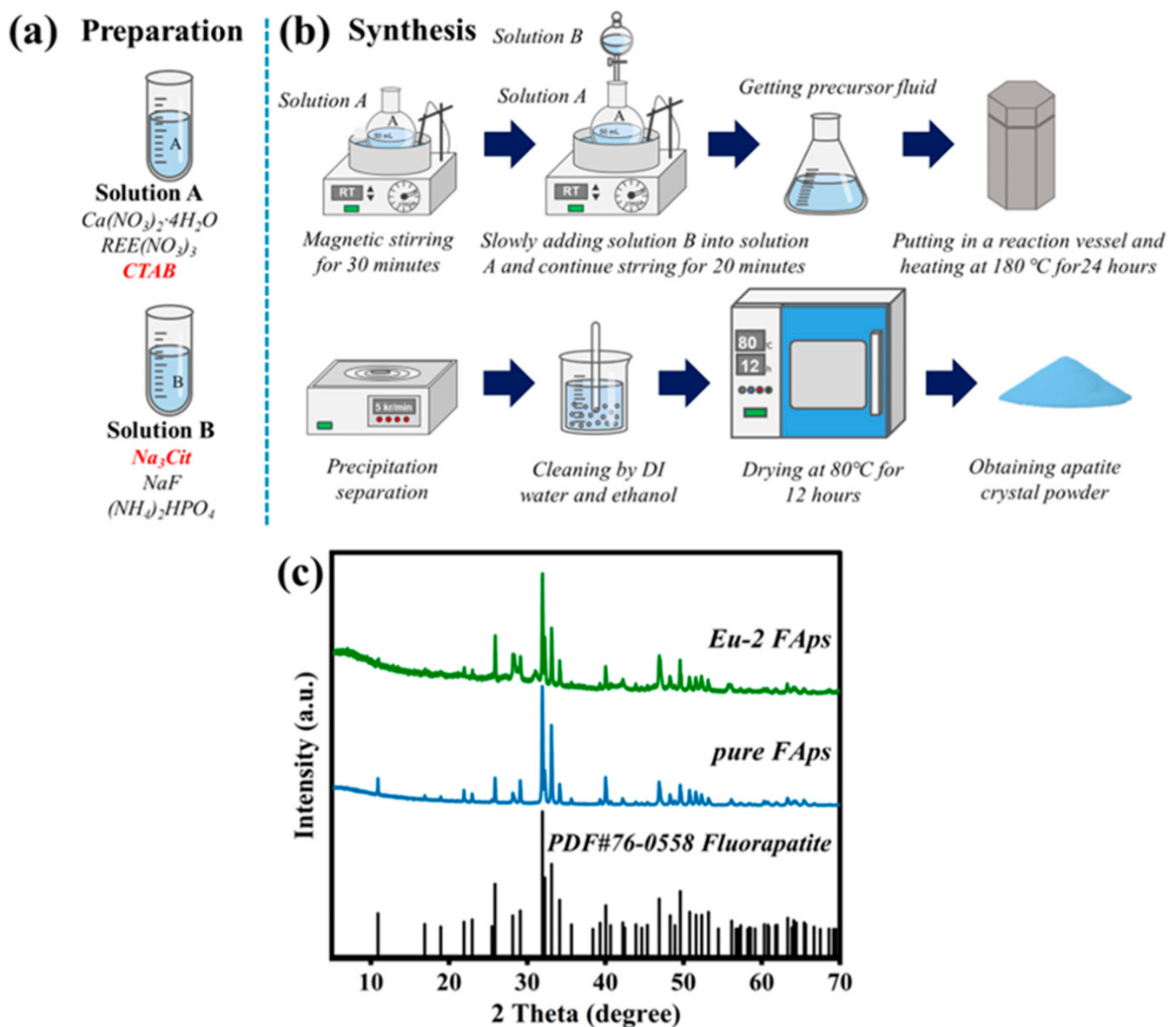


Figure 1. The flowchart showing the hydrothermal synthesizing of the REEs-doped Faps: (a) the anionic ligand and precursor solutions, (b) the hydrothermal synthesizing processing of the REEs-doped Faps, and (c) the XRD patterns of the synthesized pure and Eu-doped Faps.

Table 1. The molar quantities of the anionic ligand and precursor solutions for synthesizing the REEs-doped FApS.

Sample Number	Precursor Solution (A)			Anionic Ligand Solution (B)		
	Ca(NO ₃) ₂ ·4H ₂ O (mol/L)	REEs-Nitrate (mol/L)	CTAB (mol/L)	Na ₃ Cit·2H ₂ O (mol/L)	NaF (mol/L)	(NH ₄) ₂ HPO ₄ (mol/L)
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-2	0.098	0.002	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-4	0.096	0.004	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-6	0.094	0.006	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-8	0.092	0.008	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-10	0.09	0.01	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-12	0.088	0.012	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-14	0.086	0.014	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-16	0.084	0.016	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-18	0.082	0.018	0.03	0.267	0.267	0.111
La/Pr/Sm/Eu/Gd/Ho/Er/Yb-20	0.08	0.02	0.03	0.267	0.267	0.111

3. Results and Discussion

Figure 2 is the bright-field TEM images, EDS, and Fast Fourier Transform (FFT) spectrum of the micro-structure of the pure, La-2, Yb-2, Eu-2, and Er-2 FApS. It can be seen from the bright-field TEM images that the pure, La-2, Yb-2, Eu-2, and Er-2 FApS show an approximate rod-shaped morphology. The pure FApS show a length of approximately 3 μm and a diameter of approximately 1 μm . Compared with the pure FApS, the REEs-doped FApS show a bigger size with a larger diameter and a longer length. Among the REEs-doped FApS, the Er-2 and Eu-2 FApS show a longer length of around 10 μm and a larger diameter of 3 μm . The grain length of pure FApS is approximately 3 μm . In contrast, the La-2 and Yb-2 FApS display a size of 4 μm , while the Er-2 and Eu-2 FApS exhibit a size of around 10 μm . The EDS spectrum shows that the distribution of the Ca, P, and O elements of the pure and REEs-doped FApS is homogeneous. Similarly, the REEs are also uniformly distributed in the REEs-doped FApS, except for the area of the rare-earth fluoride nanoparticles covered on the surface of the REEs-doped FApS. For example, the flocculent aggregate morphology covered on the surface of the La-2 FApS can be observed in Figure 2b, which is the lanthanum fluoride precipitation that resulted from an inadequate interaction between La³⁺ and surfactants [24]. Additionally, the surface of the Yb-2, Eu-2, and Er-2 FApS also adhered with a small quantity of rare-earth fluoride microparticles. The high-resolution transmission electron microscopy (HRTEM) and its corresponding Fast Fourier Transform (FFT) provides solid evidence to indicate that the pure and REEs-doped FApS are single crystalline. As shown in the HRTEM images, it is interesting that all the (002) lattice planes are perpendicular to the cylindrical surface (axial direction) of the pure and REEs-doped FApS.

Figure 3 shows the interplanar spacing of the (002) lattice planes of the pure and REEs-doped FApS measured from the HRTEM images. The interplanar spacing of the (002) lattice planes of the Yb-2 FApS is about 3.38 Å, which is nearly the same as that of the pure FApS. The interplanar spacing of the (002) lattice planes of the Gd-2, Yb-2, Eu-2, and Er-2 FApS is slightly smaller than the La-2, Pr-2, Sm-2, and Ho-2 FApS. The interplanar spacing of the (002) lattice planes of the REEs-doped FApS is related to the coactions of the cationic lattice positions, atomic radius, and the effective doping concentration of the doping REEs atoms.

Figure 4 is the SEM images accompanied by EDS spectra showing the morphology, crystallite dimension, and the effective doping concentration of the La-2, Yb-2, Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FApS. It can be seen in Figure 4a–h that all the REEs-doped FApS are rodlike microparticle precipitates, which is similar with the results shown in Figure 2. The main reason for the formation of the rodlike FApS precipitates is the growth orientation of the FApS precipitates, that is, the (001) crystal direction perpendicular to (002) (as shown in Figure 2) [25]. According to the statistical result from Figure 5, the grain size

of the REEs-doped FAPs shows an average length of 4~14 μm and an average diameter of 1~4 μm . It is worth noting that the Gd-2, Ho-2, Er-2, and Eu-2 FAPs show a larger grain size, compared with that of the La-2, Yb-2, Sm-2, and Pr-2 FAPs. As shown in the EDS elements spectrum, the effective doping concentration of Yb-2 is about 0.77 mol.%, lower than that of the Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FAPs (0.9 mol.%), which demonstrated that the ratio of the effective doping concentration to the theoretical doping concentration is nearly 50%.

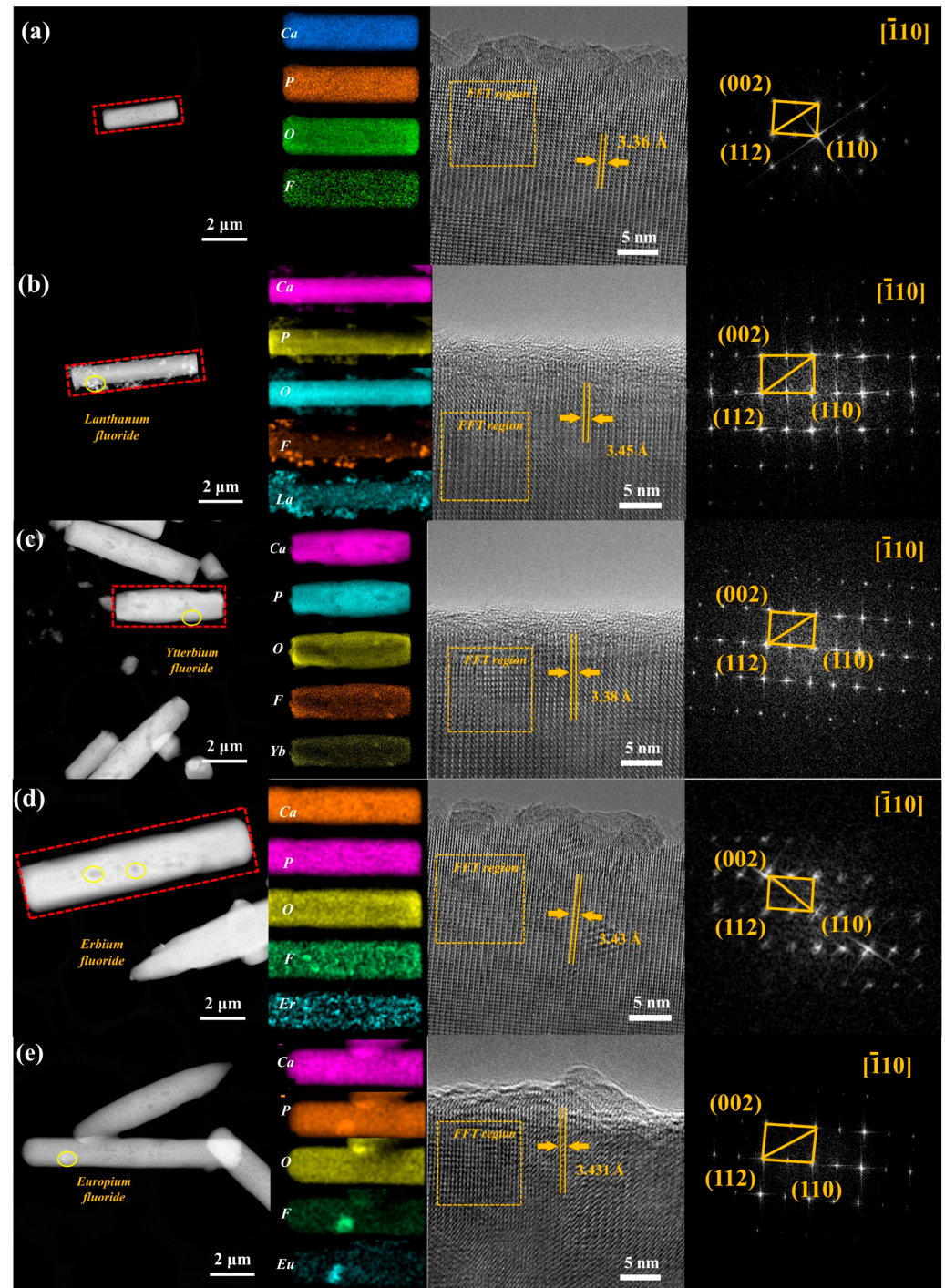


Figure 2. The TEM bright images, EDS, and FFT spectrum showing the microstructure of the (a) pure, (b) La-2, (c) Yb-2, (d) Er-2, and (e) Eu-2 FAPs.

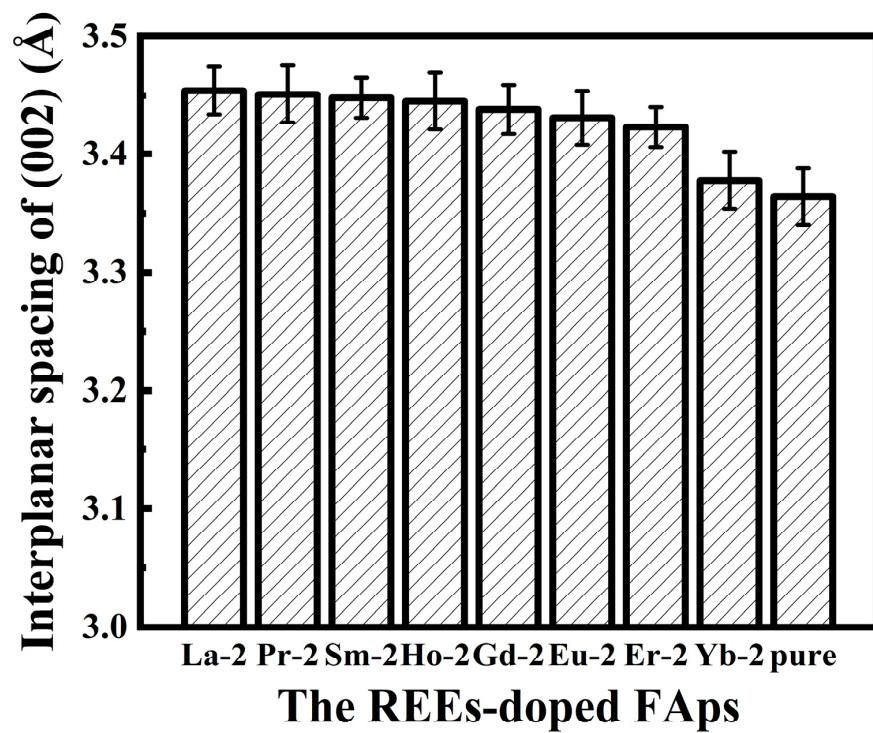


Figure 3. The interplanar spacing of the (002) lattice planes of the pure and REEs-doped FAPs.

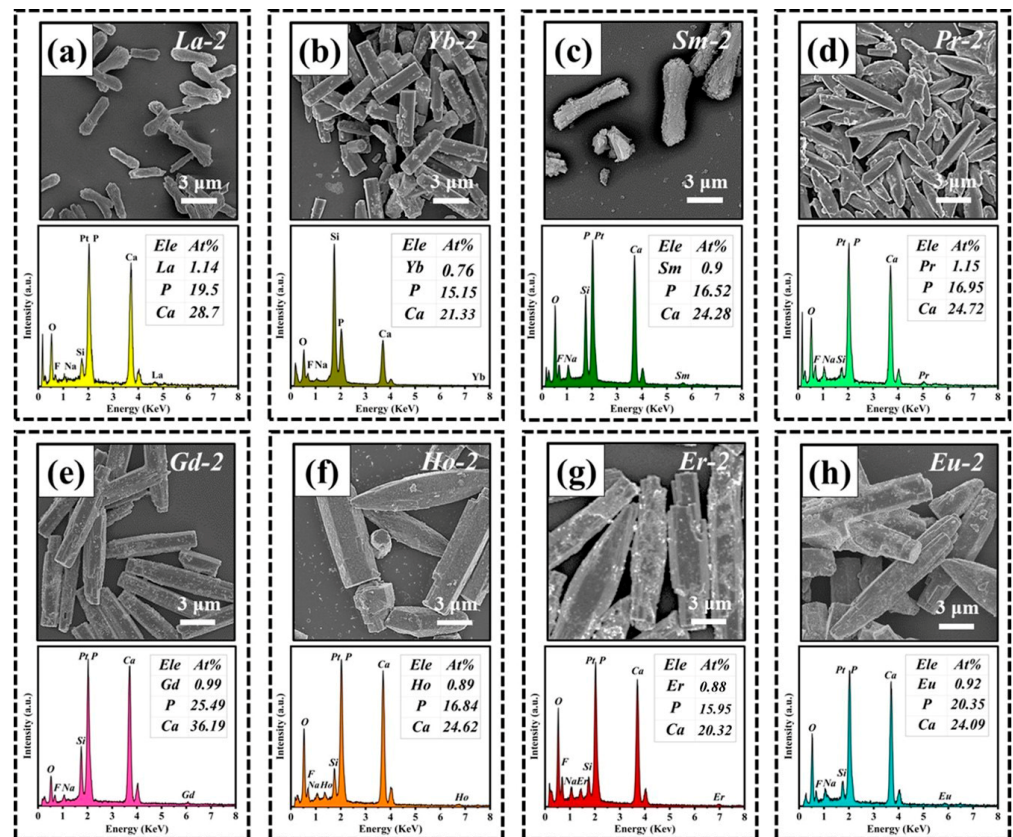


Figure 4. The SEM images accompanied by EDS spectra of the (a) La-2, (b) Yb-2, (c) Sm-2, (d) Pr-2, (e) Gd-2, (f) Ho-2, (g) Er-2, and (h) Eu-2 FAPs.

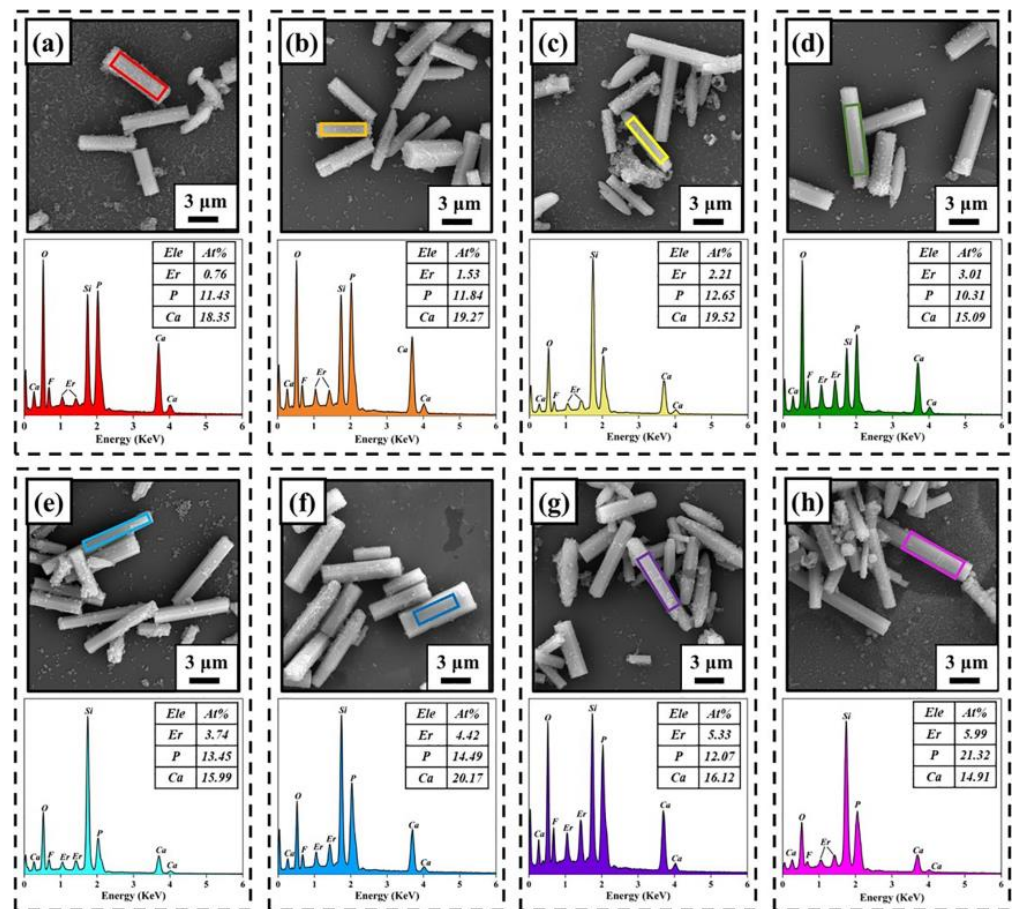


Figure 5. The SEM images accompanied by EDS spectra of the Er-doped FAPs with the Er theoretical doping concentration of (a) 2, (b) 4, (c) 6, (d) 8, (e) 10, (f) 12, (g) 14, and (h) 16 mol%.

The SEM images accompanied by EDS spectra of the Er-doped FAPs with the theoretical doping concentrations of 2, 4, 6, 8, 10, 12, 14, and 16 mol.% are shown in Figure 5. The Er-doped FAPs with the theoretical doping concentration of 2, 4, 6, 8, 10, 12, 14, and 16 mol.% all show a rod-shaped morphology. The average grain size (volume) of all the Er-doped FAPs is around $240 \mu\text{m}^3$. Nonetheless, the grain size (volume) of the Er-doped FAPs with a high concentration is a scattered, multiple-center data management group, which may result from the increasing cation concentration promoting the nucleation of the Er-doped FAPs precipitates. The effective doping concentration of Er^{3+} ions also shows a growing tendency with the increase in increasing theoretical doping concentration. The ratio of the effective doping concentration to the theoretical doping concentration of all the Er-doped FAPs is about 0.44. The obtained results showed that the increasing doping concentration of Er^{3+} ions shows no effect on the average grain size, which is similar with the results shown in ref. [26].

Figure 6 is the SEM images accompanied by EDS spectra of the Eu-doped FAPs with the Eu theoretical doping concentrations of 2, 4, 6, 8, 10, 12, 14, and 16 mol.%. Similar with the Er-doped FAPs, the shape, average grain size, and the ratio of the effective doping concentration to the theoretical doping concentration of the Eu^{3+} are free from the influence of the Eu^{3+} doping concentration. It is worth noting that a great number of rare-earth fluoride particles can be observed on the surface of the Eu-12, 14, and 16 FAPs. The amount of rare-earth fluoride particles covered on the surface of the Eu-doped FAPs also show an increase tendency with the increasing concentration of Eu^{3+} ions.

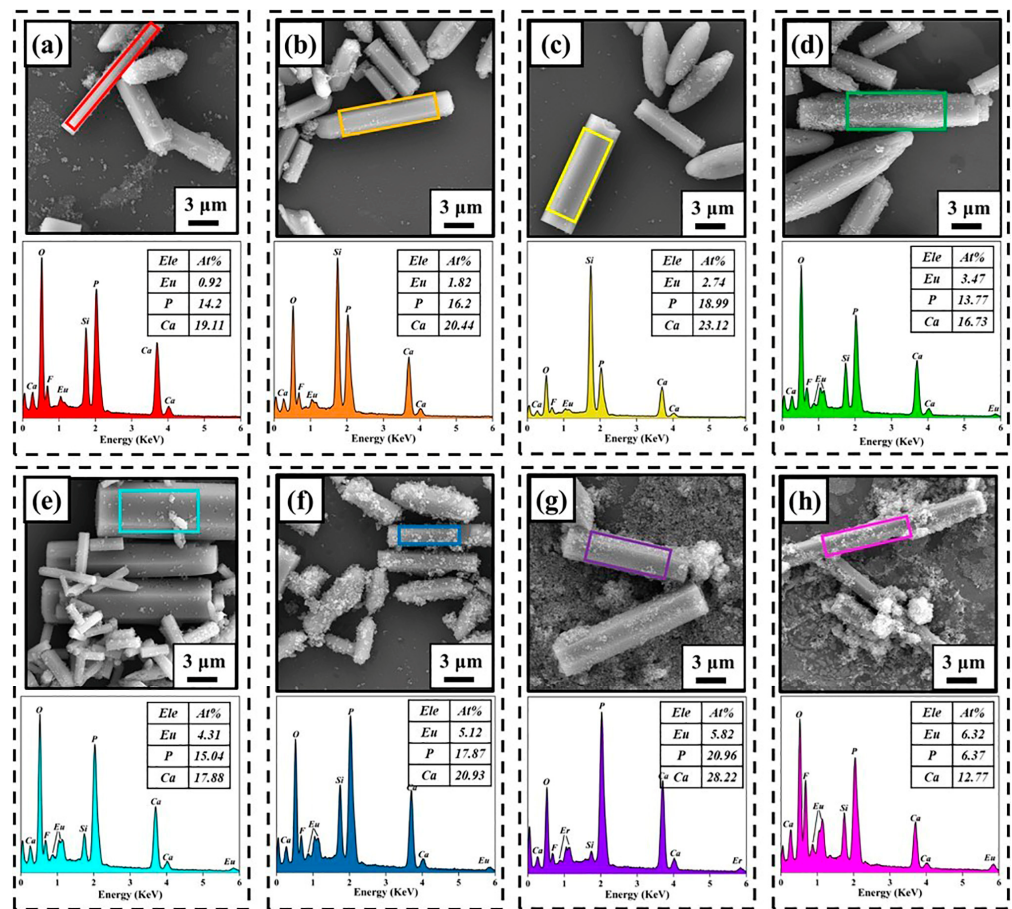


Figure 6. The SEM images accompanied by EDS spectra of the (a) Eu-2, (b) Eu-4, (c) Eu-6, (d) Eu-8, (e) Eu-10, (f) Eu-12, (g) Eu-14, and (h) Eu-16 FAPs.

Similar with the Er- and Eu-doped FAPs, the SEM images and EDS spectra of the La-, Pr-, Sm-, Gd-, Ho-, and Yb-doped FAPs also demonstrate that the REE ion doping concentration shows no effect on the average grain size. Figure 7 shows the effective doping concentration of the La-, Pr-, Sm-, Eu-, Gd-, Ho-, Er-, and Yb-doped FAPs. It can be seen that the effective doping concentration of the REEs-doped FAPs increases with the increasing theoretical doping concentration. Nevertheless, the ratio of the effective doping concentration to the theoretical doping concentration is around 50%. And this ratio gradually decreases as the theoretical doping concentration increases, like Eu-doped FAPs. The main reason is that the additions of superabundant cations are more likely to precipitate directly instead of forming REEs-doped FAPs.

Figure 8 shows the phase and crystal structure of the La-2, Yb-2, Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FAPs by the XRD patterns and the degree of (002) diffraction peak. The diffraction peaks of the REEs-doped FAPs are in good agreement with the standard spectrum peaks of the FAPs, which indicates that the formation of the phase structure of the pure and REEs FAPs. As shown in Figure 8b, the diffraction peak corresponding to the (002) crystal plane of the La-2, Yb-2, Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FAPs exhibits variable shifts, attributable to the distinct atomic radii of the dopant atoms. The red dotted line in Figure 8b represents the (002) crystal plane angle of the pure FAPs. Compared to the peak positions of the Yb-2, Gd-2, Er-2, and Eu-2 FAPs, the La-2, Sm-2, Pr-2, and Ho-2 FAPs show a visible lattice distortion.

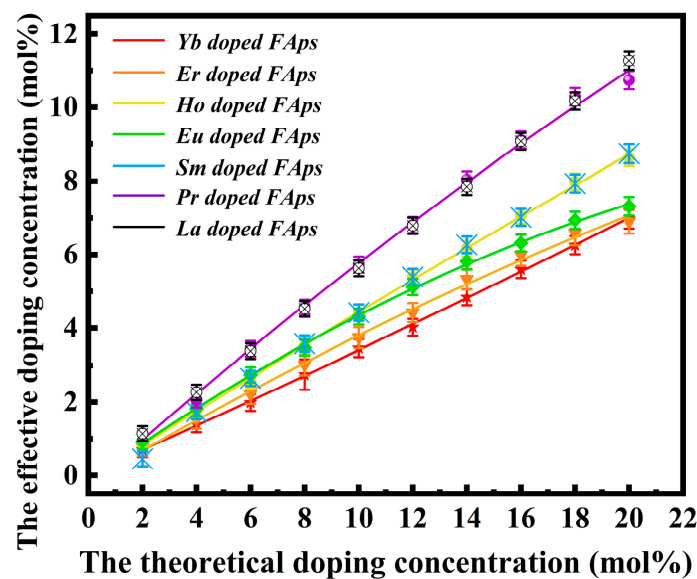


Figure 7. The effective doping concentration of the La-, Pr-, Sm-, Eu-, Gd-, Ho-, Er-, and Yb-doped FAPs.

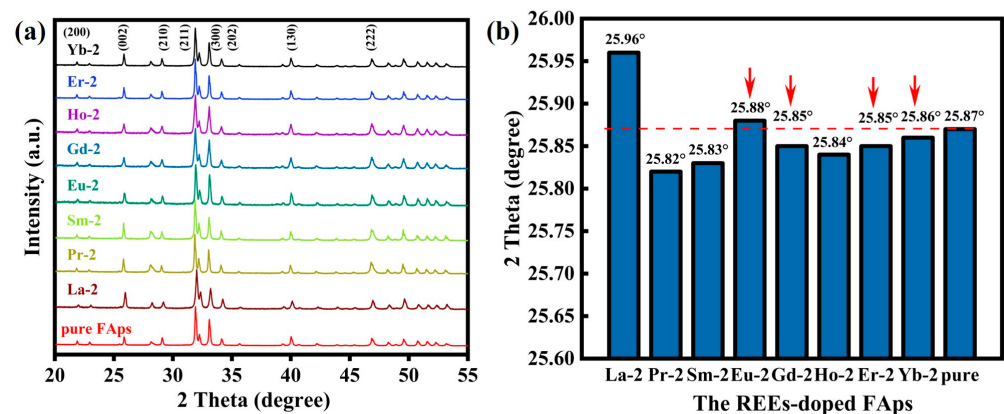


Figure 8. The phase and crystal structure of the La-2, Yb-2, Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FAPs by (a) the XRD patterns and (b) the position of (002) diffraction peak.

The XRD patterns for the Er-2, 4, 6, 8, 10, 12, 14, and 16 FAPs and Eu-2, 4, 6, 8, 10, 12, 14, and 16 FAPs are illustrated in Figure 9. It can be seen in Figure 9a,b that the Er-2, 4, 6, 8, 10, 12, 14, and 16 FAPs and Eu-2, 4, 6, 8, 10, 12, 14, and 16 FAPs can be synthesized successfully when the theoretical doping concentration is less than 20%. As the theoretical doping concentration approaches 20%, the XRD patterns of Er-16, 18, and 20 and Eu-10, 12, 14, 16, 18, and 20 FAPs show the abrupt diffraction peaks at 20.21° and 29.65° that do not belong to the FAPs phase. These diffraction peaks are analyzed to the (202) and (300) characteristic peaks of the calcium phosphate phase. The angle of the (002) diffraction peak changing with the effective doping concentration in Figure 9c,d illustrates that numerous Er^{3+} ions or Eu^{3+} ions entering the FAPs lattice led to distortion [27]. According to the Bragg Equation ($2d\sin\theta = n\lambda$), the increase in the 2-theta angle in Figure 9c,d is attributed to the decrease in interplanar crystal spacing of the (002) plane resulting from Er atom doping.

The FWHM of the (002) lattice plane in the REEs-doped FAPs is calculated in order to roughly understand the influence of the theoretical doping concentration on the lattice defects in the FAP-phase crystal. It can be seen in Figure 10 that the FWHM of REEs-doped FAPs increases with the increase in theoretical doping concentration, indicating that the degree of crystallinity gradually decreases [27]. The La-, Pr-, Sm-, and Ho-doped FAPs

show higher FWHM compared to Gd-, Er-, Eu-, Yb-doped FApS, resulting in the Gd-, Er-, Eu-, and Yb-doped FApS having better crystallinity.

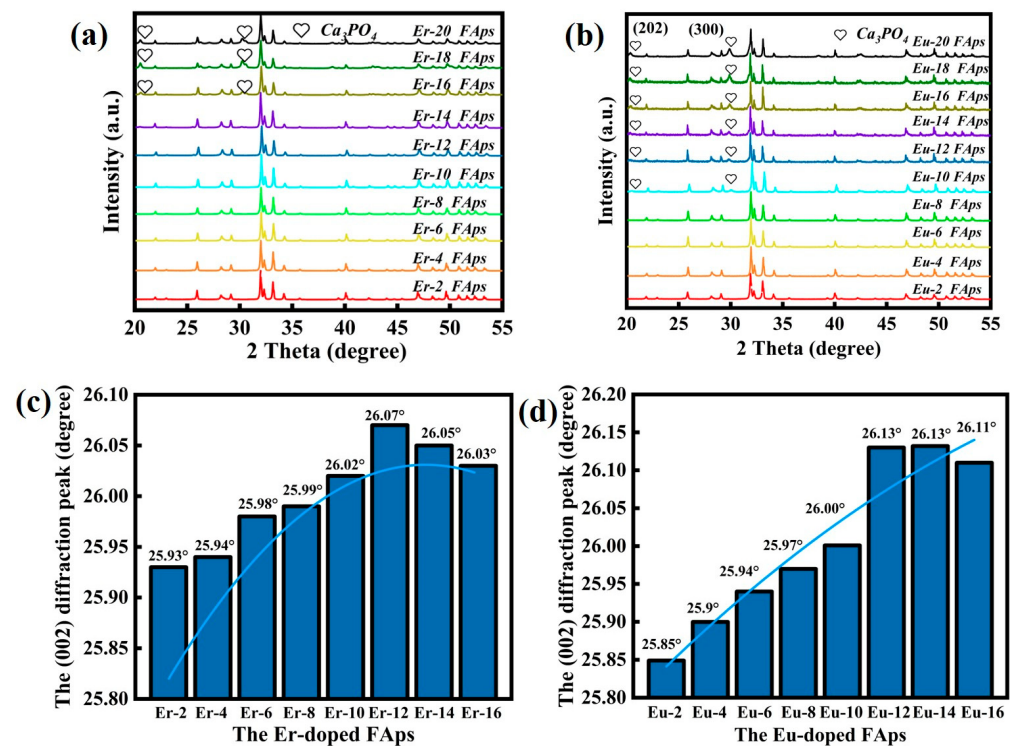


Figure 9. The phase and crystal structure of the Er-2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 and Eu-2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 by (a,b) the XRD patterns and (c,d) the position of (002) diffraction peak.

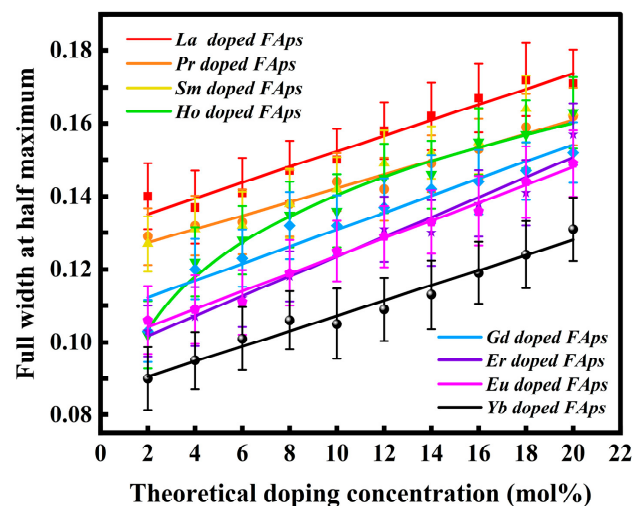


Figure 10. The FWHM of REEs-doped FApS with various theoretical doping concentrations.

The XRD patterns of REEs-doped FApS were refined, and the Rietveld calculation was performed using GSAS II to obtain the crystal structure model [28]. The Rwp of the Er-2 and Eu-2 FApS is, respectively, 8.935% and 11.448%, while the χ^2 is, respectively, 2.73% and 4.91%. The smaller error coefficient indicates that the refinement results are more reliable. From Figure 11b,c, the black cross represents the measured XRD data, the red solid line represents the XRD data fitted based on the computational structural model, the blue solid line represents the difference between the measured data and the fitted data, and the magenta columnar line represents the position of the Bragg diffraction peak. The difference

between the measured XRD diffraction peaks calculated by fitting is small and the fitting results are calculable. The refined results are listed in Table 2. Based on the crystallographic files generated by GSAS II, Vesta was used to create a lattice structure of REEs-doped FAPs, as is shown in Figure 11a. In the hexagonal crystal structure, two cationic lattice positions, namely the Ca1 and Ca2 positions, are present. Nevertheless, distinct rare-earth atoms exhibit specific tendencies for occupying these lattice positions. Notably, Er and Eu are inclined to preferentially occupy the 6h position [29]. According to the Rietveld refinements of the XRD patterns of the REEs-doped FAPs, the unit cell volume and lattice constants were calculated out and plotted in Figure 11d. Visibly, in Figure 11d, the unit cell volume and lattice constants of the Gd-2, Er-2, Eu-2, and Yb-2 FAPs are closer with the pure FAPs without REEs doping. It can be concluded that the lattice distortion of the Gd-2, Er-2, Eu-2, and Yb-2 FAPs is weaker compared with that of the Pr-2, La-2, Sm-2, and Ho-2 FAPs.

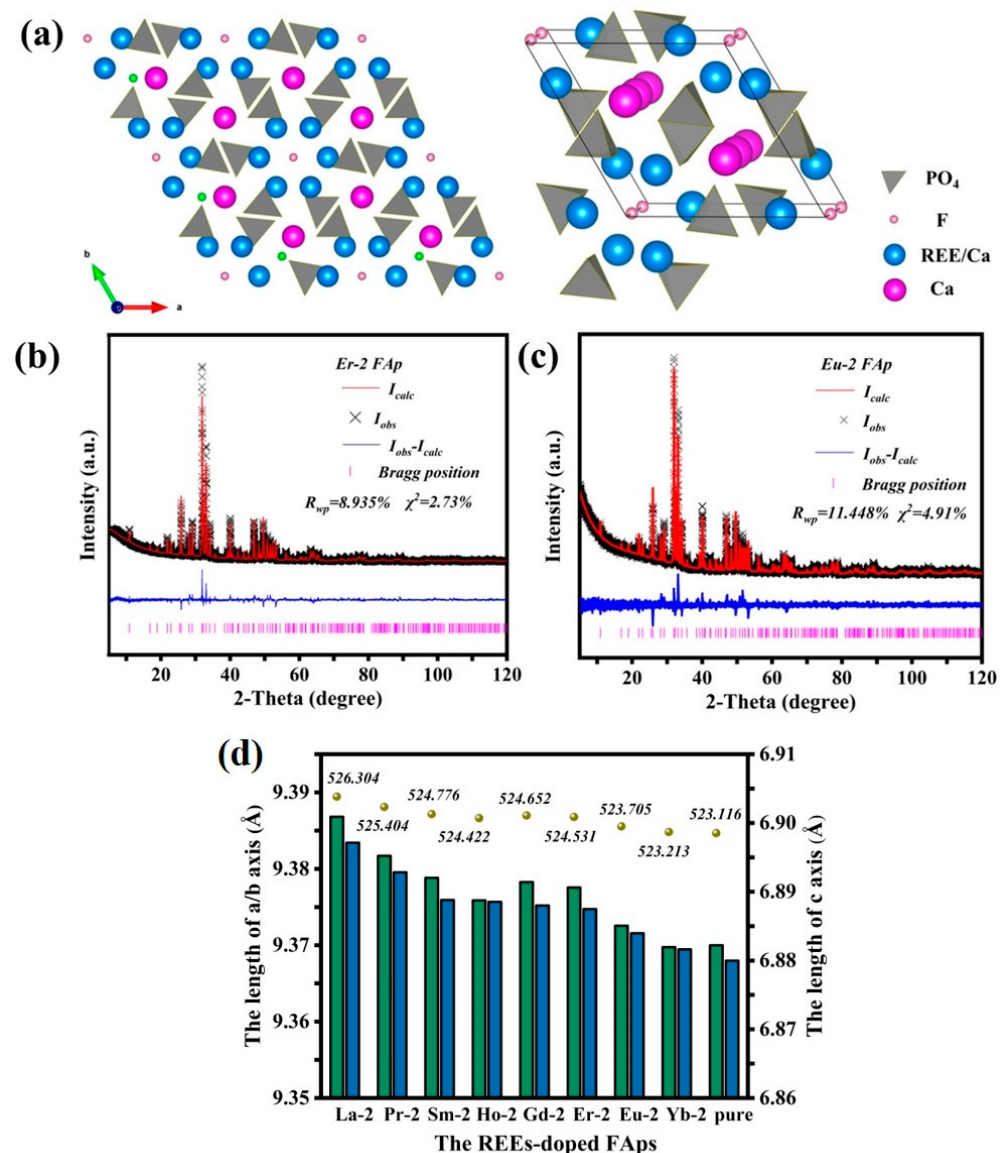


Figure 11. Refinement of La-2, Yb-2, Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FAPs: (a) lattice structure of REEs-doped FAPs (b) the Rietveld refinement of powder XRD pattern, (c) the Rietveld refinement of powder XRD pattern, and (d) the unit cell volume and lattice constants.

Trivalent rare-earth ions such as Y^{3+} and La^{3+} , which lack 4f electrons, exhibit closed electronic shells, rendering them optically inert. In contrast, other rare-earth ions possess varying numbers of electrons in the Ca1 orbit, and the transitions of these electrons gives

rise to light emission. The emission spectra are shown in Figure 12 under excitation at 250 nm. Different REEs-doped FAPs display completely different fluorescence properties.

Table 2. The crystal structure parameter of La-2, Yb-2, Sm-2, Pr-2, Gd-2, Ho-2, Er-2, and Eu-2 FAPs.

Doping Element	La	Pr	Sm	Ho	Gd	Er	Eu	Yb
Space group	P6 ₃ /m	P6 ₃ /m	P6 ₃ /m	P6 ₃ /m	P6 ₃ /m	P6 ₃ /m	P6 ₃ /m	P6 ₃ /m
Crystal system	Hex.	Hex.	Hex.	Hex.	Hex.	Hex.	Hex.	Hex.
a/b (Å)	9.38682	9.38171	9.37883	9.37588	9.37828	9.37757	9.37256	9.36976
c (Å)	6.89714	6.89285	6.88882	6.88853	6.88801	6.88749	6.88398	6.88163
α/β	90°	90°	90°	90°	90°	90°	90°	90°
γ	120°	120°	120°	120°	120°	120°	120°	120°
V (Å ³)	526.304	525.404	524.776	524.422	524.652	524.532	523.705	523.213
R _w (%)	14.207	13.859	10.215	10.451	8.295	7.322	8.936	7.742
χ^2	5.97	3.78	2.81	4.49	2.43	2.18	2.73	2.26

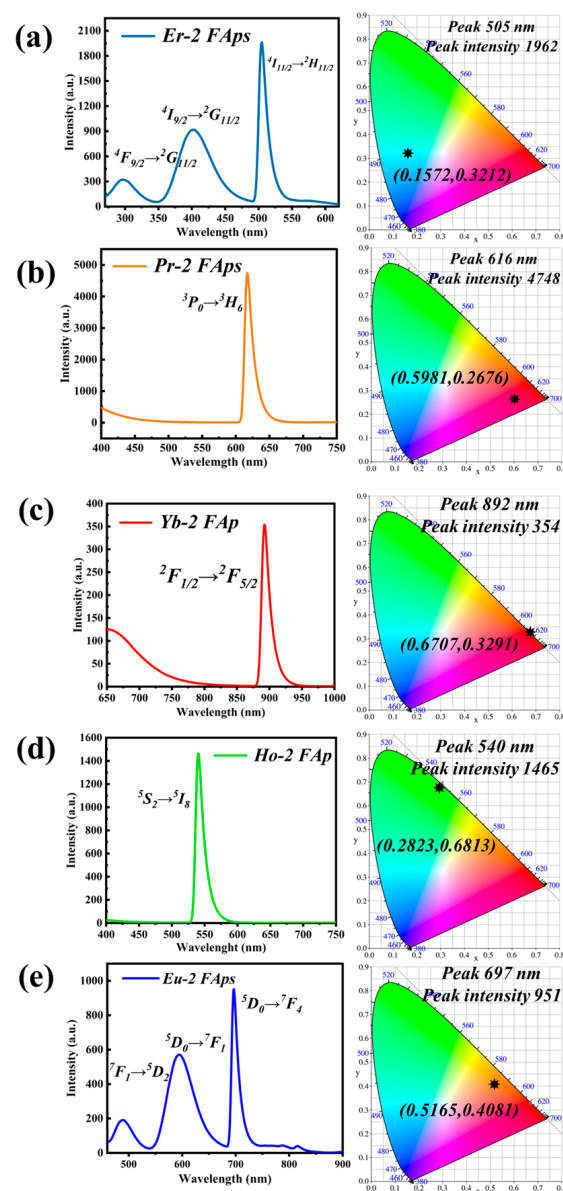


Figure 12. Fluorescence properties of Er-2/Pr-2/Yb-2/Ho-2/Eu-2 FAPs: (a–e) the emission spectrum of REEs-doped FAPs and FAPs at the wavelength of 250 nm and its corresponding CIE color co-ordinates.

It can be seen in Figure 12d that Ho-2 FAPs exhibit the emission band located at strong emission around 540 nm, which is related to the transition of $^5S_2 \rightarrow ^5I_8$. Calculating the color co-ordinates of Ho-2 FAPs based on its corresponding emission spectrum, the color of the phosphor is green. The Yb-2 and Pr-2 FAPs display emission bands, respectively, at 392 nm and 892 nm originating from the $^2F_{7/2} \rightarrow ^2F_{5/2}$ (Yb) transition in Yb and the $^5S_2 \rightarrow ^5I_8$ transition in Ho [30,31]. Figure 12a shows the emission spectra of the Er-2 FAPs, manifesting three emission bands, which feature two minor emission peaks at approximately 296 nm/401 nm and a prominent emission peak at 505 nm. These phenomena are attributed to the transitions involving $^4F_{9/2} \rightarrow ^2G_{11/2}$, $^4I_{9/2} \rightarrow ^2G_{11/2}$, and $^4I_{11/2} \rightarrow ^2H_{11/2}$, respectively [32]. In addition, Eu-2 FAPs demonstrate emissions of three bands: $^7F_1 \rightarrow ^5D_2$ (490 nm), $^5D_0 \rightarrow ^7F_1$ (594 nm), and $^5D_0 \rightarrow ^7F_4$ (697 nm) [33,34]. The CIE co-ordinates show that the Eu-2 phosphor emits orange fluorescence.

Figure 13 displays the emission spectra of Er-2, 6, 12, 16, and 20 FAPs and its changes in maximum fluorescence intensity. As shown in Figure 13b, the fluorescence emitted by the Er-2, 6, 12, 16, and 20 FAPs is mainly blue–green. By measuring the strongest fluorescence intensity at the emission band, it can be obtained that, as shown in Figure 13c–e, the fluorescence intensity first increases and then decreases as the effective doping concentration increases. Through fitting discrete points, the equation describing the change in fluorescence intensity of emitted light at 505 nm with respect to doping concentration is obtained as $y = 221.28 + 1365.57X - 107.11X^2$. By analyzing the fitting curve, it can be deduced that the optimum fluorescence intensity for the Er-doped FAPs is achieved at an effective doping concentration of 6.37 mol%. At lower concentrations, the rise in luminescence intensity can be ascribed to an augmentation in the number of luminescent centers. Conversely, the decline in luminescence intensity is attributed to excessive Er concentration, indicating concentration quenching [35].

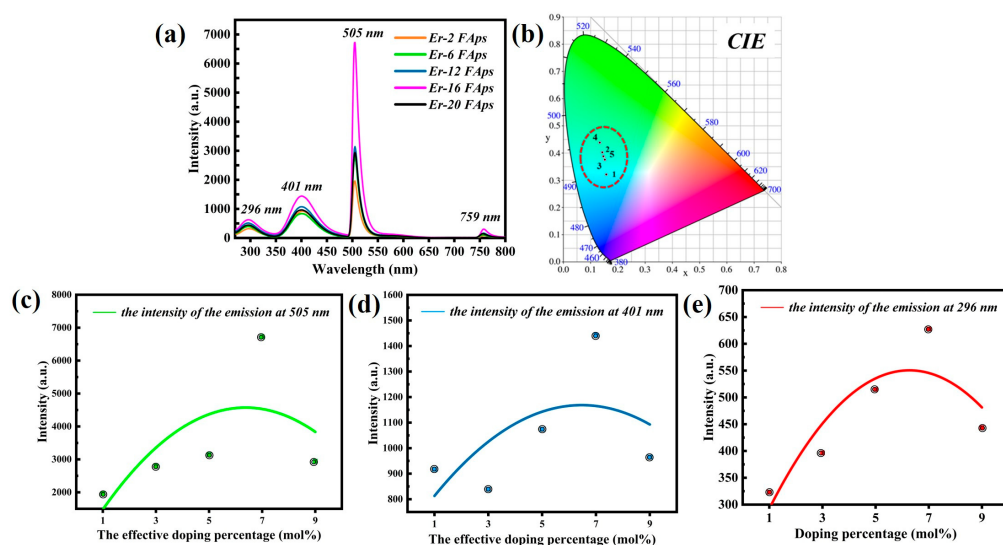


Figure 13. Fluorescence properties of Er-2, 6, 12, 16, and 20 FAPs: (a) emission spectra under excitation at 250 nm; (b) the CIE color co-ordinates; (c–e) fluorescence intensity of various emission bands (296 nm/401 nm/505 nm) changes with the effective doping concentration.

As depicted in Figure 14c–e, when excited at 250 nm, the Eu-doped FAPs phosphor exhibits three emission bands at 490 nm ($^7F_1 \rightarrow ^5D_2$), 594 nm ($^5D_0 \rightarrow ^7F_1$), and 697 nm ($^5D_0 \rightarrow ^7F_4$). The color co-ordinate diagram of the Eu-doped phosphor indicates that it emits orange light under UV lamp irradiation. In accordance with the Er-doped FAPs, the fluorescence intensity and the effective doping concentration of the Eu-doped FAPs also demonstrate a parabolic trend. The equation describing the change in fluorescence intensity with the effective doping concentration at 697 nm is determined as $y = 1394.45 + 2883.61X - 426.67X^2$. Through the

calculation of the fitting curve, it can be concluded that, when the doping concentration is 3.38 mol%, the Eu-doped FAPs with best fluorescence intensity can be obtained.

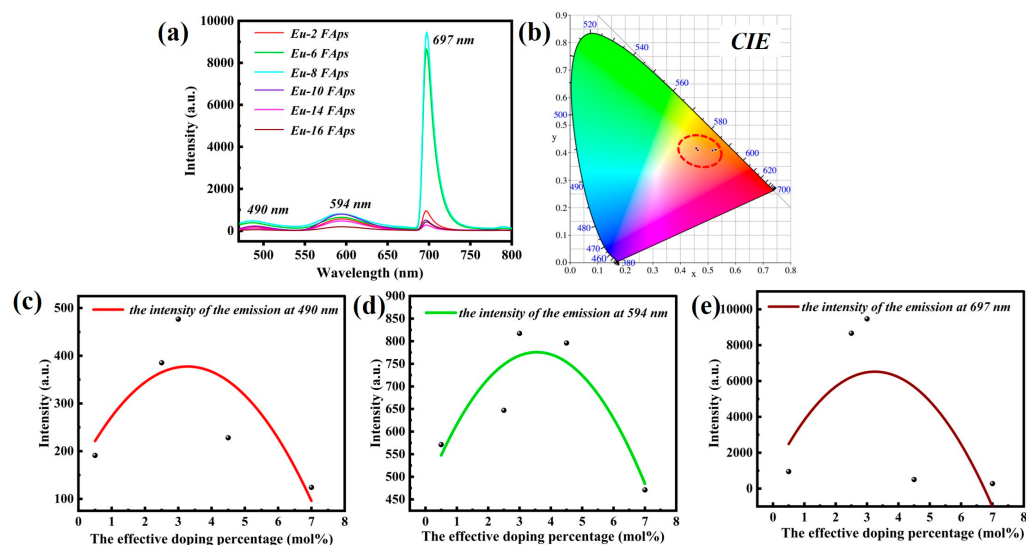


Figure 14. Fluorescence properties of Eu-2, 6, 8, 10, 14, and 16 FAPs: (a) emission spectra under excitation at 250 nm; (b) the CIE color co-ordinates; (c–e) fluorescence intensity of various emission bands (490 nm/594 nm/697 nm) changes with the effective doping concentration.

Figure 15a–c show the trend of the changes in fluorescence intensity of the Pr-, Yb-, and Ho-doped FAPs with effective doping concentration. Consistent with Eu and Er, the fluorescence intensity of Pr-, Yb-, and Ho-doped FAPs, moreover, increase first and then decreases as the effective doping concentration increases. The optimal effective doping concentrations of Pr, Yb, and Ho are 4.5, 4, and 5 mol%.

The various rare-earth atoms involve different energy levels when emitting visible light, resulting in those atoms being able to emit light of different wavelengths. For example, Er-doped FAPs emit blue–green light, while Eu-doped FAPs emit orange light, from Figure 12. When the theoretical doping concentration is 2 mol%, the (002) lattice plane FWHM of all the REE-doped FAPs is at a low value, resulting in excellent crystallinity. Instead, it can be observed in Figure 10 that the FWHM of all REE-doped FAPs is coincidentally increased with the effective doping concentration increase, which means that the crystallinity of the FAPs is gradually decreasing. High crystallinity means a well-ordered internal crystal structure, reducing energy loss from nonradiative recombination of excited electrons, which enhances the conversion of excitation energy into fluorescent radiation. Hence, an excessively high doping concentration will cause a reduction in crystallinity, leading to a decrease in fluorescence intensity. From Figures 12–15, the maximum fluorescence intensity can be found as the effective doping concentration increases to a specific threshold value. When the threshold is exceeded, the fluorescence intensity of REE-doped FAPs begins to decrease.

In addition, the FAPs crystal grains synthesized via the hydrothermal method are in the micron level in Figures 4–6, which is also beneficial to the improvement of the fluorescence intensity. This is owing to the enlarged grains with their increased surface area, which facilitate the absorption of a greater amount of excitation light energy, which leads to the excitation of a higher number of luminescent centers, thereby contributing to heightened luminescence. In contrast, the small grains cause nonradiative losses due to surface effects and reducing luminous efficiency.

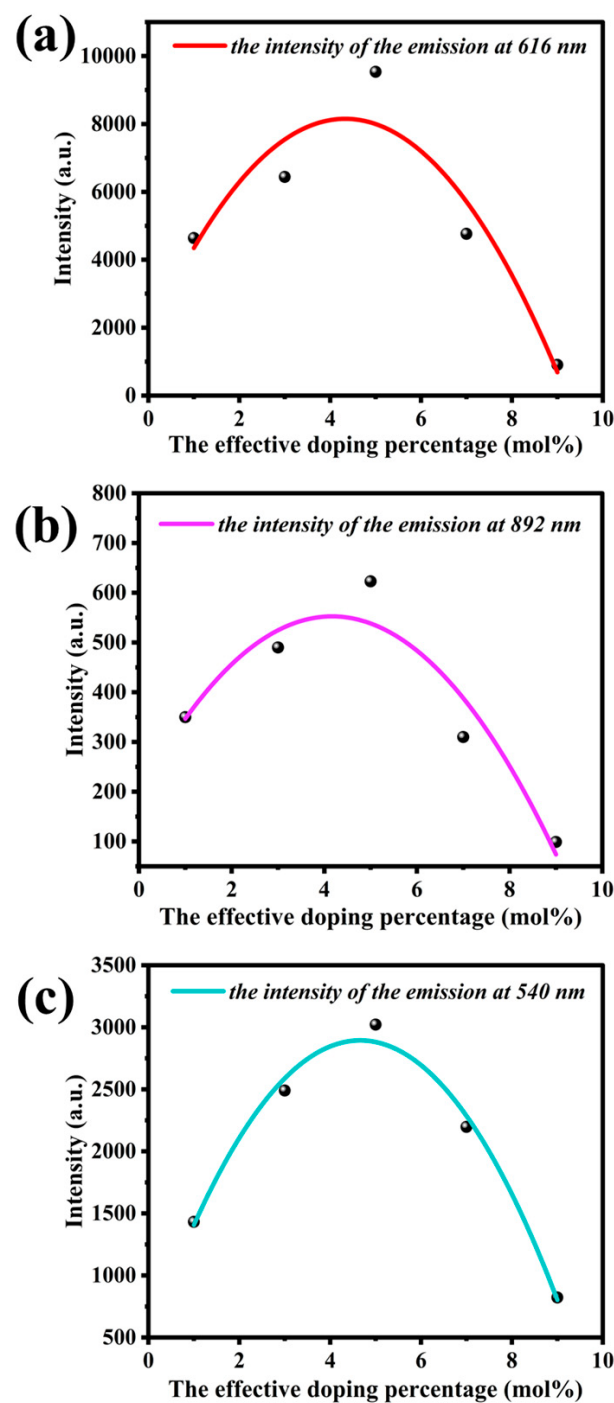


Figure 15. (a–c) The fluorescence intensity of Pr-, Yb-, and Ho-doped FAPs changes with the effective doping concentration.

4. Conclusions

The REEs-doped FAP powders synthesized by hydrothermal methods produce fluorescence of different wavelengths. Er-, Eu-, Pr-, Ho-, and Yb-doped FAPs can, respectively, emit blue, orange, red, orange, red, and green light under the excitation of ultraviolet light (250 nm). Compared with the Pr/Sm/Gd/Ho/Yb-doped FAPs, Er/Eu-doped FAPs exhibit high fluorescence intensity, attributed to their small lattice distortion, big grain size and suitable doping concentration.

The FAPs with different REE effective doping concentrations show that the fluorescence intensity increases first and then decreases as the concentration increases. This is

mainly because an increase in effective doping concentration has a positive impact on the fluorescence intensity. However, an excessively high doping concentration will lead to concentration quenching and a decrease in crystallinity, which will have a negative impact on the fluorescence intensity. Therefore, when the doping concentration of Er is at 6.37 mol%, Eu is at 3.38 mol%, Pr is at 4.5 mol%, Yb is at 4 mol%, and Ho is at 5 mol%, the combination of good crystallinity, higher luminescent atoms, and larger grain size results in excellent fluorescence intensity.

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