

Red-emitting transparent Eu³⁺-doped fluorapatite ceramics

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Abstract

Transparent red-emitting ceramics have attracted considerable attention for advanced optical technologies, yet their practical applications remain limited. In the search for new optical materials, there is increasing interest in achieving transparency in non-cubic systems; here, we explored the fabrication of red-emitting ceramics using fluorapatite, a non-cubic host. Eu^{3+} -doped calcium and strontium fluorapatite (Eu^{3+} :FAP and Eu^{3+} :S-FAP, respectively) ceramics were synthesized via a wet-chemical route and spark plasma sintering. The ceramics sintered at 950 °C exhibited the highest transparency, achieving in-line transmittances of 81.2% and 72.9% at the red wavelength of 619 nm, and grain sizes of 98 and 153 nm, respectively. High-resolution transmission electron microscopy confirmed that the grain boundaries and triple junctions were free of melts and other inclusions that could cause light scattering. Optical characterization revealed strong excitation around 460 nm and sharp red emissions corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (~580 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (~620 nm) transitions of Eu^{3+} . The fluorescence lifetimes of Eu^{3+} :FAP and Eu^{3+} :S-FAP were 0.5 and 0.87 ms, respectively. These results demonstrate the potential of transparent red-emitting Eu^{3+} -doped fluorapatite ceramics for solid-state lighting and biophotonics.

Keywords

Transparent ceramics, apatite, phosphors, spark plasma sintering, optical materials/properties

1. Introduction

Apatite is a mineral group with a wide range of compositions and the general formula $M_{10}(ZO_4)_6X_2$ ($M = Ca, Sr, Ba$; $Z = P, V$; $X = F, OH, Cl$).¹ Among them, calcium hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) and fluorapatite (FAP; $Ca_{10}(PO_4)_6F_2$) have been extensively studied as representative biomaterials, due to their excellent biocompatibility, particularly for bone and dental applications.²⁻⁴ More recently, transparent bulk HAP and FAP ceramics⁵⁻¹⁰ are promising for tissue engineering applications, enabling real-time visualization of living cells and dynamic monitoring of bone regeneration.^{11, 12}

In addition to biomedical applications, apatite materials have demonstrated potential as host matrices for optical materials such as phosphors and lasers. Among them, FAP is considered more suitable than HAP for various optical applications.¹³ This is mainly due to the absence of OH groups that cause quenching through energy transfer between rare earth (RE) ions and OH ions.^{14, 15} Moreover, the ionic radii of Ca^{2+} and Sr^{2+} in the FAP lattice closely match those of luminescent trivalent RE (RE^{3+}) ions, allowing ion

substitution.¹⁶ Consequently, a variety of RE³⁺-doped FAP phosphors have been developed and exhibited characteristic fluorescence derived from *4f-4f* or *4f-5d* electronic transitions.^{17–25}

Among the various RE ions, trivalent europium (Eu³⁺) exhibits sharp red emission with a narrow spectral width, ensuring high color purity and stability. While Eu²⁺ is widely used²⁶, particularly in nitrides such as CaAlSiN₃:Eu²⁺ for its intense and broadband emission^{27, 28}, recent advances in Eu³⁺-doped transparent oxide ceramics (e.g., Y₂O₃²⁹, YAG³⁰) have demonstrated their potential for high-color-purity red emission and stable optical performance. Eu³⁺-doped fluorapatite (FAP) is especially promising because of its excellent fluorescence characteristics and suitability for applications ranging from optical devices to biophotonics, where red emission offers reduced scattering and greater tissue penetration than shorter-wavelength visible light. This combination of optical and biological advantages positions Eu³⁺:FAP as a distinctive transparent red-emitting ceramic phosphor.

To realize this potential, however, fabricating fully transparent Eu³⁺:FAP ceramics remains challenging due to the non-cubic crystal structure of FAP, where grain-boundary scattering (γ_{gb}), along with pores and secondary phases, degrades the optical quality. While numerous studies have examined Eu³⁺:FAP in the form of powder phosphors^{18, 20},

^{23, 31}, reports on fully transparent bulk ceramics are scarce. In recent years, efforts have been made to develop transparent red-emitting ceramics. For example, Zheng et al.³¹ synthesized ~20-nm Eu³⁺-doped strontium FAP (Sr₁₀(PO₄)₆F₂, abbreviated as S-FAP) nanoparticles using a wet-chemical method and attempted to fabricate transparent ceramics by densifying these powders through vacuum hot pressing. Building on this progress, the present study aimed to enhance the visible-light transparency of Eu³⁺:FAP ceramics to reduce scattering, supporting their application in emerging photonic and biomedical technologies.

For overcoming transparency limitations of non-cubic ceramics, grain size (d) reduction is a key strategy. According to the Rayleigh–Gans–Debye theory, γ_{gb} is given by the following equation:³²

$$\gamma_{gb}(\lambda) = \frac{3\pi^2 d \Delta n^2}{2\lambda^2} \quad (1)$$

where λ , d , and Δn represent the wavelength of the incident light, the average grain size of the ceramics, and the average refractive-index difference at grain boundaries, respectively. This theory is applicable in the Rayleigh scattering regime ($d \ll \lambda$) and the transition region ($d \approx \lambda$) and has been experimentally validated by the successful synthesis of transparent FAP ceramics using advanced ceramic processing techniques.

In this study, we developed two types of transparent red-emitting ceramics, Eu^{3+} :FAP and Eu^{3+} :S-FAP, by combining a wet-chemical route for fine particle synthesis with spark plasma sintering (SPS), which enables rapid, low-temperature densification and suppresses grain growth. The optimal sintering temperatures for Eu^{3+} :FAP ceramics were systematically investigated, and their microstructure, transmittance, and fluorescence properties were evaluated. As a result, we achieved the first demonstration of transparent Eu^{3+} :FAP ceramics, which reached an in-line transmittance of 81.2% at 619 nm. For Eu^{3+} :S-FAP ceramics, the in-line transmittance was 72.9% at 619 nm, significantly higher than the ~40% previously reported for transparent S-FAP ceramics.

2. Materials and Methods

Figure 1 illustrates the fabrication process for Eu^{3+} :FAP and Eu^{3+} :S-FAP ceramic samples. Powder preparation and sintering are the two main steps. Powder preparation consists of precursor synthesis, fluorination, and calcination. The synthesized powders were densified using an SPS machine. The optimal sintering temperature was first determined for Eu^{3+} :FAP and then applied to Eu^{3+} :S-FAP. The material properties of the obtained Eu^{3+} :FAP and Eu^{3+} :S-FAP samples were evaluated, including phase identification and microstructural observation. In addition, their optical properties such as transmittance and fluorescence, were evaluated.

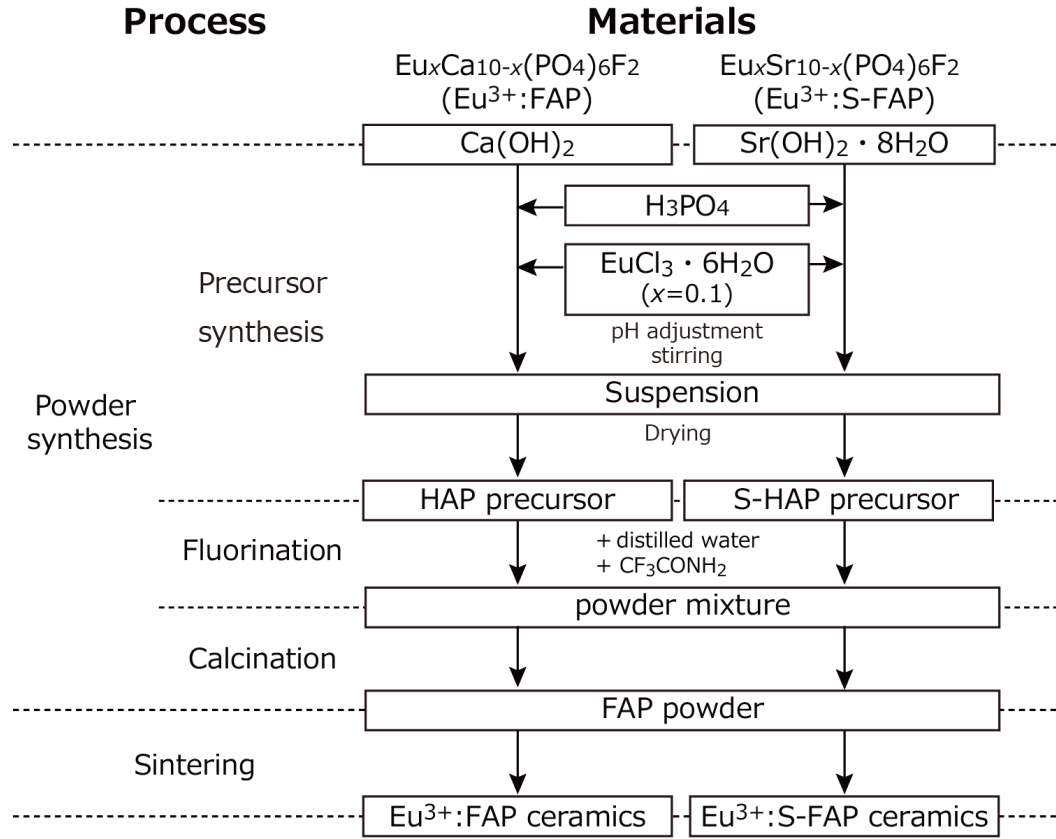


Figure 1. Schematic diagram of the synthesis process for transparent red-emitting

$\text{Eu}^{3+}:\text{FAP}$ and $\text{Eu}^{3+}:\text{S-FAP}$ ceramics.

2.1 Powder preparation

Calcium hydroxide ($\geq 99.9\%$ purity, Kanto Chemical), phosphoric acid (85 wt.% in H_2O , Kishida Chemical), and europium chloride hydrate (99.99% purity, Sigma-Aldrich) were used as starting materials to synthesize $\text{Eu}^{3+}:\text{FAP}$ powders via a wet-chemical route. First, each material was separately dissolved in deionized water. After stirring, the phosphoric acid aqueous solution was slowly added to the calcium hydroxide slurry to synthesize a

precursor for HAP. Subsequently, the europium chloride hydrate solution was added to achieve an Eu doping concentration of 1 at.%. The precursor for strontium hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$: S-HAP) was synthesized using the same procedure, except that calcium hydroxide was replaced with strontium hydroxide octahydrate (99.995% purity, Sigma–Aldrich). The resulting precipitate was washed with deionized water, recovered by filtration, and subsequently dried in an oven at 60°C to obtain HAP and S-HAP. Next, HAP and S-HAP were fluorinated by mixing with trifluoroacetamide (>98.0%, Tokyo Chemical Industry Co. Ltd.). After a second drying process, the obtained Eu^{3+} :FAP and Eu^{3+} :S-FAP were calcined for 2 h under atmospheric conditions at 800 and 600°C, respectively.

2.2 Sintering

The synthesized powders were sieved and then densified using an SPS machine (LABOX-315, Sinterland, Japan) to obtain highly dense, fine-grained Eu^{3+} :FAP ceramics. The powder was poured into a graphite mold with an inner diameter of 10 mm and sintered under uniaxial pressure. A carbon sheet was placed between the powder and graphite mold to enhance conduction efficiency from the electrodes. The sintering temperature was monitored using a pyrometer positioned over a pin hole on the surface of the graphite mold.

To examine the effects of temperature on the optical properties and grain growth of the ceramics, sintering was conducted on Eu^{3+} :FAP at various temperatures between 850 and 1100°C at intervals of approximately 50°C. The Eu^{3+} :S-FAP ceramics were sintered at 950°C, one of the identified optimal temperatures for Eu^{3+} :FAP at which both microstructural densification and optical transmittance were maximized. In all experiments, the heating rate, applied pressure, and holding time were fixed at 5°C/min, 80 MPa, and 20 min, respectively. To prevent sample cracking due to thermal shock during the cooling process, the temperature was decreased at a rate of 20°C/min. Finally, sintered disks with a diameter of 10 mm and a thickness of approximately 1.5 mm were obtained.

2.3 Material characterization

The calcined powders were analyzed by X-ray diffraction (XRD; RINT-TTR III, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) from a source operated at 40 kV and 150 mA. The powder morphology and sintered microstructure were observed by scanning electron microscopy (SEM; S-4800, Hitachi, Japan). For microstructural observation, the samples were mirror-polished and thermally etched at approximately 100°C below the sintering temperature to expose the grain boundaries. The grain size

was measured using the following analysis of SEM images. The contours of more than 300 grains were manually outlined for each sample, and their cross-sectional areas (S) were determined using ImageJ software (National Institutes of Health, NIH) as described elsewhere.⁴⁰ The area-equivalent circle diameter (g) was calculated using the formula $g = \sqrt{4S/\pi}$, and the grain size (d) was estimated as $d = 1.225g$, assuming spherical grains.³² The aspect ratio was evaluated from the major-to-minor axis ratio of ellipses fitted to the traced grain outlines. Owing to the high density of the sintered materials, differences in porosity could not be detected using Archimedes' method. Therefore, porosity was evaluated by analyzing the areal fraction of pores relative to grains in the SEM images. Thin specimens for transmission electron microscopy (TEM) analysis were prepared by mechanical polishing to a thickness of <0.1 mm, followed by ion milling at ~1 kV using a PIPS II system (Gatan Inc., USA) to achieve electron transparency. To prevent charging, the specimens were coated with a thin carbon layer. TEM observations were conducted using a 200 kV microscope (JEM-2010F, JEOL, Japan).

2.4 Optical characterization

For optical measurements, the sintered body was carefully mirror-polished on both

sides using diamond slurry. After polishing, the Eu^{3+} :FAP ceramics had thicknesses ranging from 1.2 to 1.6 mm, while the Eu^{3+} :S-FAP ceramics were polished to 1.1 mm. The thickness L of each specimen was measured using a micrometer screw gauge and used in the subsequent calculation of optical loss coefficients.

The optical in-line transmittance spectra $T(\lambda)$ were measured over the wavelength range of 300–1700 nm using a UV/VIS/NIR spectrometer (UV-3600Plus, Shimadzu, Japan). To enable reliable comparison among samples of different thicknesses, we evaluated the total loss coefficient $\delta(\lambda)$, including both the absorption and scattering losses, from the measured transmittance spectra using the following equation:

$$T(\lambda)_L = (1 - R_{\text{th}}(\lambda))^2 \exp(-\delta(\lambda)L) \quad (2)$$

In Equation (2), the reflectance R_{th} was theoretically derived from the refractive index dispersion n of an undoped FAP single crystal, following the relationship $R = \frac{(1 - n)^2}{(1 + n)^2}$.⁴¹ Using the obtained $\delta(\lambda)$ values, we estimated the normalized transmission spectrum for a sample with a standard thickness of 1.0 mm, denoted as $T_{1.0}(\lambda)$.

Excitation spectra in the wavelength range of 250–500 nm and fluorescence spectra from 500 to 750 nm at an excitation wavelength of 460 nm were measured using an optical spectrum analyzer (FLS1000-SD-stm, Edinburgh Instruments, UK) equipped with a xenon arc steady-state/flash lamp as the excitation source. The fluorescence

lifetime was calculated from the time-dependent fluorescence decay curve at 630 nm, which was obtained using a photodetector at an excitation wavelength of 465 nm at room temperature.

3. Results and discussion

3.1 Eu^{3+} :FAP and Eu^{3+} :S-FAP powders

Figures 2A and 2B show SEM images of the synthesized Eu^{3+} :FAP and Eu^{3+} :S-FAP powders. The morphologies of the synthesized particles were spherical to elliptical, with aspect ratios ranging from 1.5 to 1.6, which was consistent with those of previously reported nanopowders prepared via hydrothermal²³ or co-precipitation³¹ methods. The median particle size based on 300 particles was 52.3 nm for Eu^{3+} :FAP and 40.3 nm for Eu^{3+} :S-FAP. The difference in particle size is attributed to the difference in calcination temperature (800 and 600°C, respectively).

Figures 2C and 2D show the XRD patterns of Eu^{3+} :FAP and Eu^{3+} :S-FAP powders, which are consistent with the standard patterns of FAP (PDF# 01-071-0881) and S-FAP (PDF# 00-050-1744), respectively. These results confirm that the synthesized powders consisted of a single phase, with no detectable peaks from residual reagents or reaction intermediates.

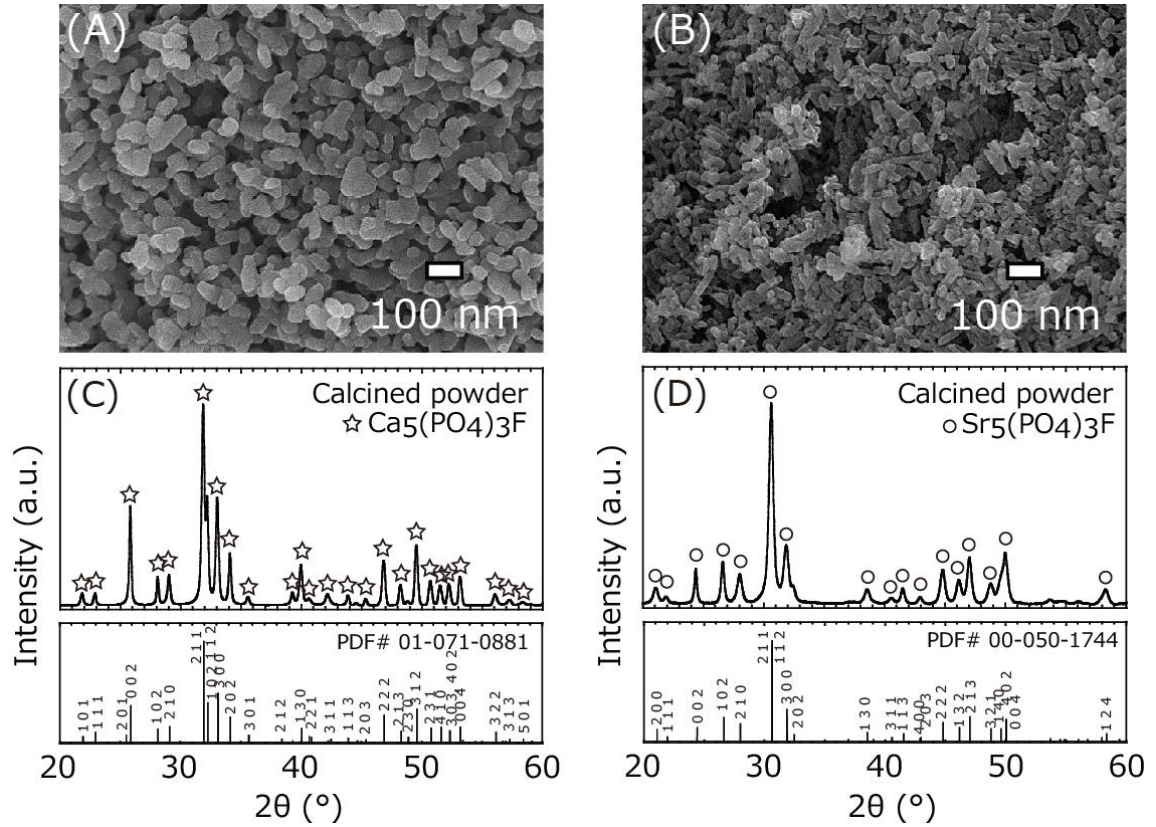


Figure 2. SEM images of the synthesized (A) Eu^{3+} :FAP and (B) Eu^{3+} :S-FAP powders.

XRD patterns of the (C) Eu^{3+} :FAP and (D) Eu^{3+} :S-FAP powders.

3.2 Eu^{3+} :FAP ceramics

3.2.1 Optical transmittance

Figure 3 shows the appearance of Eu^{3+} :FAP ceramics sintered at temperatures ranging from 850°C to 1100°C. The samples changed from opaque to transparent with increasing sintering temperature. The maximum transparency was observed at 900°C and 950°C. Above 1000°C the sample gradually became opaque from the center, and

the entire sample was opaque at 1100°C. In previous studies, a typical temperature of 1150°C was employed in conventional electric furnaces²¹ and SPS²⁵ to achieve high densification, but some residual pores a few micrometers in size were still observed in the microstructures. In contrast, in this study densification was achieved at a relatively lower temperature (200°C), and the resulting ceramics exhibited significantly higher transparency.

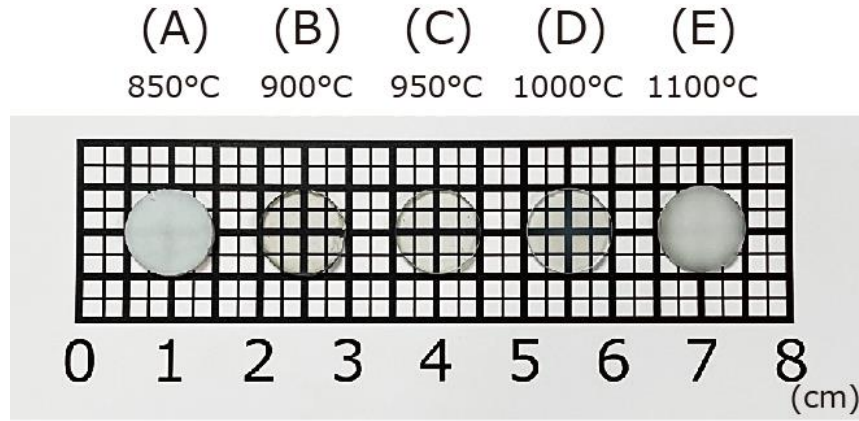


Figure 3. Photographs of Eu^{3+} :FAP ceramics sintered for 20 min at (A) 850°C, (B) 900°C, (C) 950°C, (D) 1000°C, and (E) 1100°C. Representative appearance of samples mirror-polished on both sides. The ruled lines in the background have a 0.25-mm pitch.

Figure 4A shows the in-line transmittance (T) spectra in the UV-Vis-NIR region for Eu^{3+} :FAP ceramics sintered at temperatures ranging from 850°C to 1100°C. The black dashed line represents the theoretical transmittance calculated using the Sellmeier coefficient, which was experimentally determined from measurements of the refractive

index dispersion of single-crystal fluorapatite.⁴¹ Ceramic samples sintered at both 900 and 950°C exhibited high and very similar transmittance. Their T values exceeded 78% at 500 nm and increased at higher wavelengths, approaching the theoretical transmittance in the near-infrared region. These high transmittance values are comparable to that of our previously reported FAP ceramics without RE doping¹⁰ as well as those doped with RE ions such as Yb,³⁷ Nd³⁸, and Ce.³⁹

Absorption bands attributed to doped Eu^{3+} ions were observed in the wavelength range of 400–600 nm.⁴² A weak OH^- absorption band was detected at 1435 nm and attributed to a trace amount of residual HAP precursor.¹⁰ This can potentially be eliminated by improving the fluorination process. At the red emission wavelength of 619 nm, which corresponds to the strongest emission peak of Eu^{3+} ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition), the Eu^{3+} :FAP ceramic sintered at 950°C exhibited the highest transmittance of 81.2% (Figure 4A).

Figure 4B shows the in-line transmittance spectra of Eu^{3+} :S-FAP ceramics. The transmittance exceeded 70% at 600 nm, increased at higher wavelengths, and approached the theoretical transmittance in the near-infrared region. This transmittance is higher than that reported by Zheng et al.³¹ for Eu^{3+} :S-FAP ceramics densified by vacuum hot-pressing. Similar to the Eu^{3+} :FAP samples, absorption bands corresponding

to doped Eu^{3+} ions were also observed for the Eu^{3+} :S-FAP samples at 400–600 nm.

These results confirmed the substitution of Eu^{3+} ions into the Ca or Sr sites within the FAP or S-FAP structures. No OH^- -related absorption was observed at 1435 nm, indicating that the Eu^{3+} :S-FAP samples were sufficiently fluorinated. At the red emission wavelength of 619 nm, the transmittance of Eu^{3+} :S-FAP was 72.9%, which is significantly higher than that reported for Eu^{3+} -doped samples with 2 and 3 at% in a previous study ($\sim 40\%$).³¹ Because no noticeable quenching effects were observed at these concentrations, comparing the transmittance values is reasonable. The enhanced in-line transmittance, particularly in the visible region, is attributed to successful densification at a lower temperature and a shorter holding time, which suppressed grain growth compared with the previous study. The total loss coefficient (δ) was 1.97 cm^{-1} , which was lower than that of the Eu^{3+} :FAP sample sintered at the same temperature. The reason for this difference is discussed in Section 3.2.2.

Figure 4C shows the total loss coefficient in the 400–600 nm wavelength range. The Eu^{3+} :FAP sample exhibited absorption bands due to luminescent Eu^{3+} ions at 459, 527, and 573 nm. In comparison, the Eu^{3+} :S-FAP sample exhibited slightly blue-shifted absorption bands, likely due to differences in the host lattice.

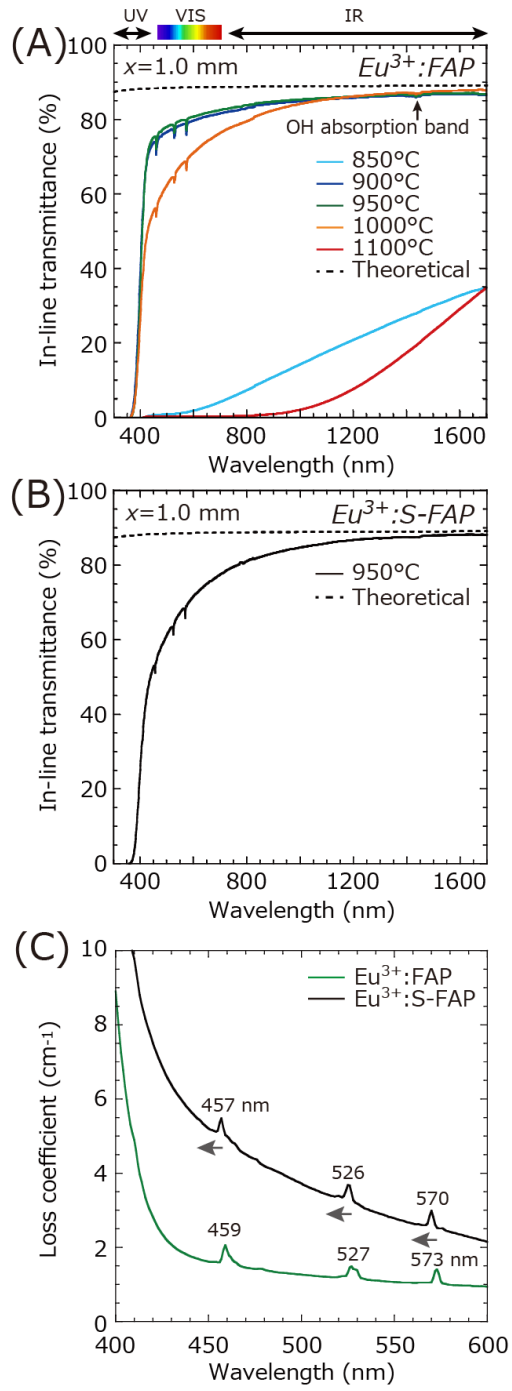


Figure 4. In-line transmittance spectra of (A) $\text{Eu}^{3+}:\text{FAP}$ and (B) $\text{Eu}^{3+}:\text{S-FAP}$ ceramics.

(C) Loss coefficients of $\text{Eu}^{3+}:\text{FAP}$ and $\text{Eu}^{3+}:\text{S-FAP}$ ceramics.

3.2.2 Microstructure

Figures 5A–E show field emission-SEM images of Eu^{3+} :FAP ceramics sintered at various temperatures. The average grain size increased with the sintering temperature (60, 85, 98, 138, and 494 nm at 850, 900, 950, 1000, and 1100°C, respectively). No secondary phases were detected in any of the samples. Although the sample sintered at 850°C exhibited the smallest grain size, there were isolated or interconnected residual pores at the grain boundaries and triple junctions (indicated by white arrows in the figure). This is thought to be the main cause of the opaque appearance of this sample (see Figure 4A) and explains the significant increase in transmittance observed between 850 and 900°C, where densification was largely completed and pores were eliminated. In contrast, the samples sintered at 900°C and above exhibited highly dense microstructures with residual porosity of <0.01 vol.%, and excellent transparency, as shown in Figures. 3B, 3C, and 4A. Meanwhile, the sample sintered at 1000°C exhibited slight opacity in the central region, and that sintered at 1100°C appeared opaque throughout. This degradation in optical transmittance at higher temperatures is attributed to increased light scattering caused by either birefringence due to grain growth or the coalescence and enlargement of residual pores through aggregation. Although not observed across the entire sample, aggregated residual pores were occasionally found in certain regions under low-magnification SEM

observation, which may have contributed to the reduced transmittance at 1100 °C.

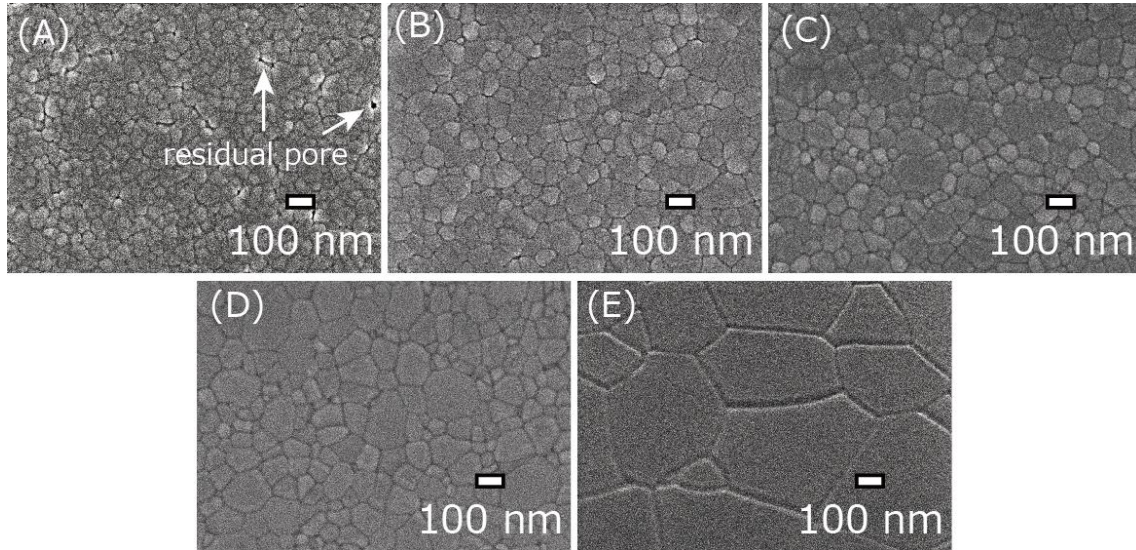


Figure 5. SEM images of Eu^{3+} :FAP ceramics sintered at (A) 850°C, (B) 900°C, (C) 950°C, (D) 1000°C, and (E) 1100°C. All samples were sintered for 20 min under a compressive load of 80 MPa. White arrows indicate residual pores. Scale bar: 100 nm.

Figure 6 shows the microstructure of Eu^{3+} :S-FAP ceramics sintered at 950°C, which was the optimal sintering temperature determined for Eu^{3+} :FAP. The average grain size of Eu^{3+} :S-FAP was 153 nm, approximately 1.6 times that of Eu^{3+} :FAP obtained under the same sintering conditions. Microstructural observation revealed intragranular residual pores (white arrows in Figure 6), which explain the slightly lower in-line transmittance of Eu^{3+} :S-FAP ceramics in the visible region (Figure 4B)

compared to that of Eu^{3+} :FAP. The presence of these intragranular pores suggests that grain boundary migration proceeded more rapidly in Eu^{3+} :S-FAP. This enhanced sinterability of Eu^{3+} :S-FAP was likely due to the lower calcination temperature used to prepare the corresponding powder, which resulted in smaller particle sizes at the start of sintering. Therefore, further optimization of the sintering temperature of Eu^{3+} :S-FAP ceramics may help reduce intra-grain pores in the microstructure and improve optical transmittance.

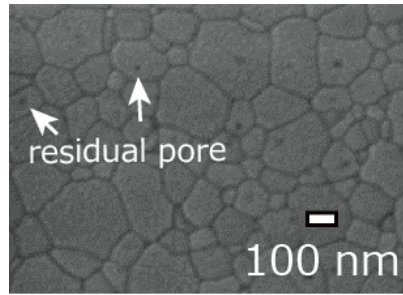


Figure 6. SEM image of the Eu^{3+} :S-FAP ceramic sintered at 950°C for 20 min under a compressive load of 80 MPa. White arrows indicate residual pores. Scale bar: 100 nm.

Figure 7A shows a TEM image of Eu^{3+} :FAP ceramics sintered at 950°C . TEM provide high-resolution images of the sample microstructure without unwanted influence from thermal etching. No precipitates or dislocations were observed in the intragranular region, indicating a relatively uniform microstructure. Analysis of the TEM images revealed an average grain size (d) of 110 nm, which was nearly identical

to that measured from the SEM image. This suggests that thermal etching for SEM observation did not cause significant grain growth. Only a few residual pores were observed within the crystalline grains, each less than 10 nm in diameter (indicated by arrows in the figure). The high-resolution TEM (HR-TEM) image acquired under edge-on conditions (Figure 7B) showed no evidence of precipitates, pores, melt, or secondary phases at the triple junctions. The typical lattice spacing of $\text{Eu}^{3+}\text{:FAP}$ measured from image analysis was 0.36 nm, which is similar to the (002) lattice spacing of FAP.

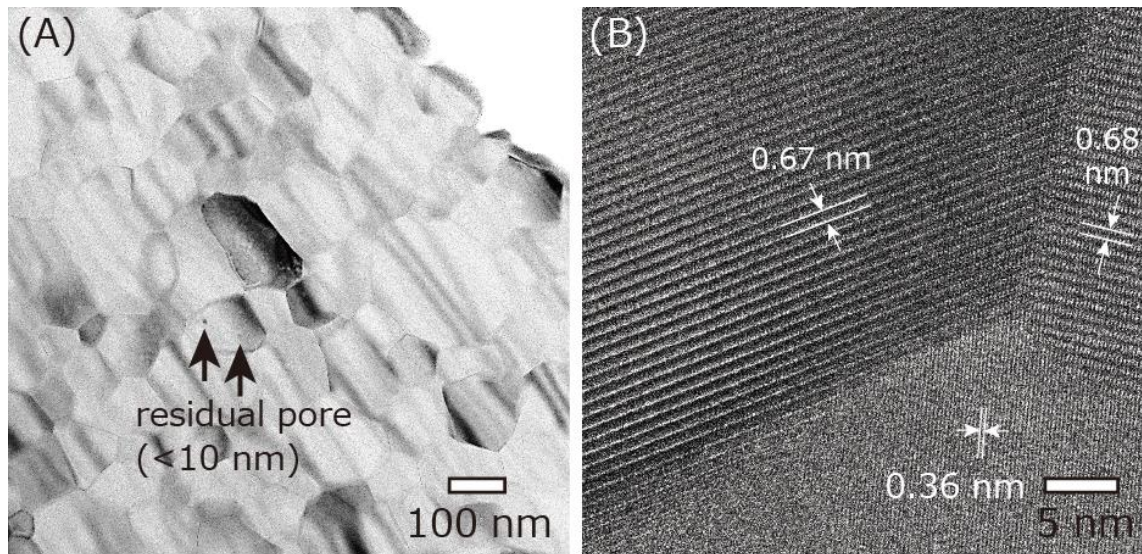


Figure 7. (A) TEM bright field image and (B) HR-TEM image at the triple junction of transparent $\text{Eu}^{3+}\text{:FAP}$ ceramics sintered at 950°C for 20 min. Black arrows indicate residual pores.

3.2.3 Fluorescence properties

Figures 8A and 8B show photographs of Eu^{3+} :FAP and Eu^{3+} :S-FAP ceramics sintered at 950°C, respectively. In each panel, the upper images were acquired under natural light, and the lower ones were acquired under UV light. Both ceramics exhibited warm luminescent colors, although the brightness of the emitted light differed. The sintering temperature of 950°C was selected for both compositions because it provided the highest optical transparency for Eu^{3+} :FAP, and it was also applied to Eu^{3+} :S-FAP to allow a direct comparison of luminescence behavior under identical processing conditions.

Figure 8C shows the measured fluorescence spectra of Eu^{3+} :FAP ceramics sintered at 850–1100°C. The excitation spectra displayed the same pattern regardless of the sintering temperature, with a peak at 465 nm. The excitation peaks observed at 394, 411, 464, and 479 nm are assigned to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^5\text{D}_3$, ${}^5\text{D}_2$, and ${}^5\text{D}_1$ transitions of Eu^{3+} , respectively. Notably, the 411-nm peak (${}^5\text{D}_3$) is more intense than the 394-nm peak (${}^5\text{L}_6$) in the FAP host, suggesting an influence of the local crystal field. The emission spectrum excited at 465 nm exhibited sharp peaks from Eu^{3+} ions around 570 and 620 nm, which is clearly distinct from the emission pattern of Eu^{2+} . Although only the 250–500 nm range is shown in Figure 8C, we also measured the excitation spectrum of

Eu³⁺:FAP down to 210 nm. In this extended range, a charge transfer band (CTB) is clearly observed around 220–240 nm, confirming the presence of this feature in Eu³⁺:FAP. This result is consistent with predictions based on the size effect,⁴³ suggesting that Eu³⁺ is preferentially incorporated over Eu²⁺ because of its closer match in ionic radius to the 7-coordinated Ca (II) site in the FAP structure (ionic radius: 1.06 Å). Following the substitution with Eu³⁺, charge balance is presumably maintained primarily through the introduction of cation vacancies ($2\text{Eu}^{3+} + [\text{v}] \rightleftharpoons 3\text{Ca}^{2+}$)⁴⁴ or in part by the supply of O²⁻ from water or reagents during the synthesis of HAP precursor ($\text{Ca}^{2+} + \text{F}^- \rightleftharpoons \text{Eu}^{3+} + \text{O}^{2-}$).⁴⁵ The obtained fluorescence spectrum is consistent with that of Eu³⁺:FAP reported in previous studies,^{21, 23} where the ⁵D₀ → ⁷F₂ transition occurs preferentially over the ⁵D₀ → ⁷F₁ transition. Furthermore, the emission intensity at 630 nm, corresponding to the ⁵D₀ → ⁷F₂ electric dipole transition of Eu³⁺, was slightly higher at lower sintering temperatures (850–950°C), remained stable up to 1000°C, and decreased selectively at 1100°C. This trend indicates that a higher sintering temperature induces a more symmetric local environment surrounding Eu³⁺ ions, suppressing the ⁵D₀ → ⁷F₂ transition, which is highly sensitive to local structural asymmetry. In contrast, other transitions such as ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₄ remained largely unaffected, indicating that they are less sensitive to the crystal field symmetry. Owing to the

influence of scattering, direct comparison of fluorescence intensities among samples with differing transmittance is not straightforward. More accurate assessment using integrating sphere measurements is left for future studies.

Figure 8D shows the fluorescence spectrum of the Eu^{3+} :S-FAP ceramics under 461 nm excitation. The excitation spectrum exhibits several characteristic peaks, notably at 394, 411, and 460 nm, corresponding respectively to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^5\text{D}_3$, and ${}^5\text{D}_2$ transitions of Eu^{3+} . Additional peaks at 363, 383, and 399 nm are attributed to the ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^5\text{G}_3/{}^5\text{L}_7$, and ${}^5\text{L}_7/{}^5\text{L}_8$ transitions. These spectral features reflect differences in the crystal field environment and site symmetry compared to the Ca-based host. The maximum fluorescence intensity appears around 620 nm, which is consistent with previous studies on Eu^{3+} :S-FAP fine powder³¹ and Eu^{3+} :S-FAP transparent glass.⁴⁶

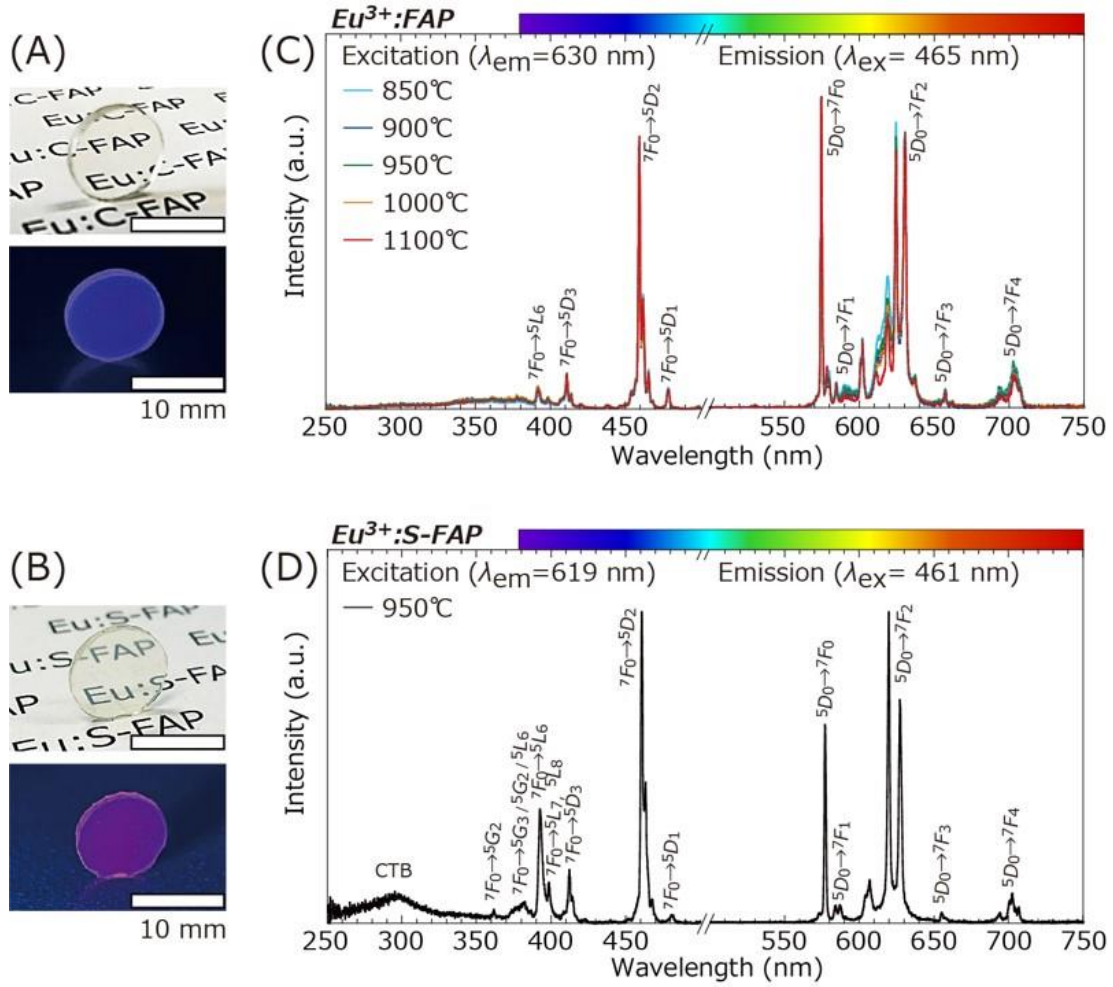


Figure 8. Photographs of (A) $\text{Eu}^{3+}:\text{FAP}$ and (B) $\text{Eu}^{3+}:\text{S-FAP}$ transparent red-emitting ceramics under natural light (top) and UV light (bottom), and photoluminescence spectra of (C) $\text{Eu}^{3+}:\text{FAP}$ and (D) $\text{Eu}^{3+}:\text{S-FAP}$.

Figures 9A and 9B show the fluorescence decay curves of the $\text{Eu}^{3+}:\text{FAP}$ and $\text{Eu}^{3+}:\text{S-FAP}$ ceramics, respectively. The curve for $\text{Eu}^{3+}:\text{FAP}$ was well-fitted with a double-exponential function independent of the sintering temperature:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (3)$$

where $I(t)$ denotes the fluorescence intensity at time t , A_1 and A_2 are the relative amplitudes of the two components, and τ_1 and τ_2 are the corresponding fluorescence lifetimes. The average lifetime (τ) of transparent red-emitting Eu^{3+} :FAP ceramics was calculated as follows:⁴⁷

$$\tau = \frac{(A_1\tau_1^2 + A_2\tau_2^2)}{(A_1\tau_1 + A_2\tau_2)} \quad (4)$$

In contrast, the fluorescence decay of Eu^{3+} :S-FAP ceramics was fitted using a single exponential function:

$$I(t) = A \exp\left(-\frac{t}{\tau}\right) \quad (5)$$

The calculated lifetimes of Eu^{3+} :FAP and Eu^{3+} :S-FAP were 0.50 and 0.87 ms, respectively. Quenching due to residual OH from the HAP precursor was observed in Eu^{3+} :FAP. This issue may be addressed in the future by optimizing the fluorination process to achieve complete conversion of the precursor.

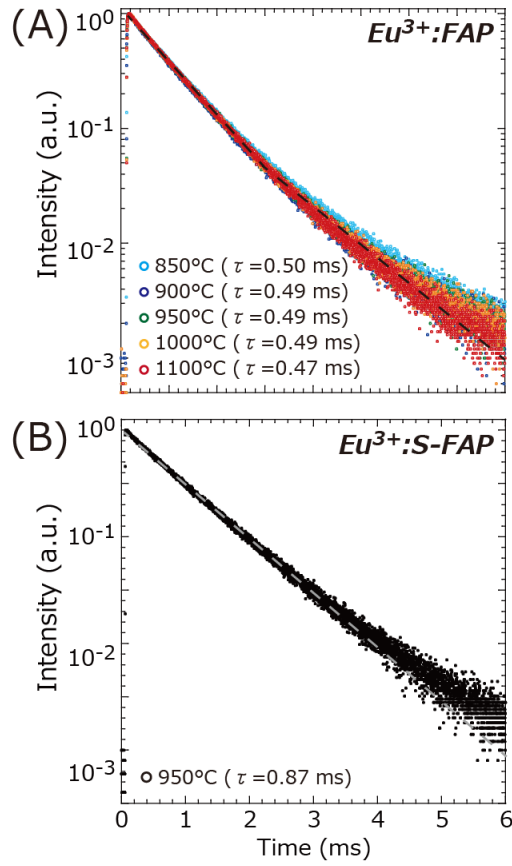


Figure 9. Fluorescence decay of (A) $Eu^{3+}:FAP$ and (B) $Eu^{3+}:S-FAP$ transparent red-emitting ceramics.

To further highlight the advantages of our materials, we compared them with representative Eu-doped transparent red-emitting ceramics, as shown in Table 1. Despite their non-cubic structure, the present $Eu^{3+}:FAP$ and $Eu^{3+}:S-FAP$ ceramics exhibited high in-line transmittance and low-temperature densification (~ 950 °C). These results confirm the effectiveness of our synthesis approach and support the potential of apatite-based ceramics as efficient luminescent materials for integration into photonic devices and biophotonic platforms.

Table 1. Optical Properties of Eu³⁺-doped transparent red-emitting ceramics

λ_{em} : emission wavelength, λ_{ex} : excitation wavelength, T_{th} : in-line transmission, L : sample thickness, $T_{sint.}$: sintering temperature, τ : lifetime, HP: hot pressing, CS: conventional sintering method

Host	Dopant	Doping (at.%)	λ_{em} (nm)	λ_{ex} (nm)	T_{th} at 0.62 μm (%)	L (mm)	$T_{sint.}$ (°C)	Sintering method	τ (ms)	Reference
FAP	Eu ³⁺	1	630	465	81	1.0	950	SPS	0.5	This study
S-FAP	Eu ³⁺	1	619	461	73	1.0	950	SPS	0.87	This study
S-FAP	Eu ³⁺	2, 3	616	465	~40	2.0	1150	HP	2.1-2.3	[31]
Y ₂ O ₃	Eu ³⁺	5	620	282	70	2.5	1580	HP	N.A.	[29]
YAG	Eu ³⁺	1	591	395	82	1.7	1780	CS	3.5	[30]

4. Conclusions

This study demonstrated the successful fabrication of transparent red-emitting Eu³⁺:FAP ceramics exhibiting sharp red emission under blue light excitation. While achieving optical transparency in non-cubic ceramics is inherently challenging because of grain boundary scattering, we addressed this issue by synthesizing single-phase powders with an average particle size of 52 nm via a wet-chemical route, followed by densification at 950°C using SPS. The resulting Eu³⁺:FAP and Eu³⁺:S-FAP ceramics exhibited in-line transmittances of 81.2% and 72.9% at 619 nm, respectively representing the highest reported values for these materials. In addition to their high transparency, the materials exhibited spectrally stable, sharp-line red emission characteristic of Eu³⁺, indicating their potential candidates for applications in high-color-rendering lighting, integrated photonic devices, and bio-optical components. Further optimization of the doping concentrations

and sintering conditions is expected to improve their optical properties.

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