Sr5(PO4)3OH, which subsequently transforms to the initial formation of amorphous strontium phosphate and analysis showed that the reaction mechanism evolves via crystallisation of β-SrHPO4 through the formation of Sr3H2(PO4)3·2H2O as an intermediate. Furthermore, in situ analysis of aliquots revealed favourable crystallisation of β-SrHPO4, including synchrotron-based X-ray diffraction (XRD) analysis, luminescence of Ce3+ and Eu3+ dopants, light transmission, reflectance, and thermogravimetry to track structural changes in SrHPO4 under different experimental conditions. Ex situ analysis of aliquots revealed favourable crystallisation of β-SrHPO4, through the formation of Sr3H2(PO4)3·2H2O as an intermediate. Furthermore, in situ analysis showed that the reaction mechanism evolves via the initial formation of amorphous strontium phosphate and Sr3(PO4)2·OH, which subsequently transforms to γ-SrHPO4. Analysis of the luminescence properties of the lanthanide dopants provided insights into the coordination environments of the substituted Sr2+ sites.

Crystallisation of phosphates revisited: a multi-step formation process for SrHPO4

Abstract: SrHPO4 is used in a multitude of applications, including biomedicine, catalysts, luminescent materials, and batteries. However, the performance of these materials depends on the ability to control the formation and transformation of strontium phosphates. This work focuses on the application of in situ and ex situ measurements, including synchrotron-based X-ray diffraction (XRD) analysis, luminescence of Ce3+ and Eu3+ dopants, light transmission, reflectance, and thermogravimetry to track structural changes in SrHPO4 under different experimental conditions. Ex situ analysis of aliquots revealed favourable crystallisation of β-SrHPO4, through the formation of Sr3H2(PO4)3·2H2O as an intermediate. Furthermore, in situ analysis showed that the reaction mechanism evolves via the initial formation of amorphous strontium phosphate and Sr3(PO4)2·OH, which subsequently transforms to γ-SrHPO4. Analysis of the luminescence properties of the lanthanide dopants provided insights into the coordination environments of the substituted Sr2+ sites.

Keywords: in situ luminescence; lanthanides; SrHPO4; synchrotron radiation; X-ray diffraction.

1 Introduction

In recent years, SrHPO4 has been applied in a wide variety of fields, such as bone cements [1], drug delivery [2], immobilisation of heavy-metal ions [3, 4], catalysis [5], luminescent compounds [6], and battery material coatings [7]. Among these applications, special attention has been paid to the use of strontium phosphates in biomedicine as a means of improving or substituting calcium phosphate compounds in bone regeneration [8]. In comparison to calcium phosphates, strontium phosphates have been reported to have better bioaffinity, which improves the proliferation of bone stem cells [2]. However, biomedical applications depend on the stability of phosphate-based compounds in aqueous solutions, which has motivated many research groups to study the transformation between different phosphate phases, primarily focusing on calcium-based compounds [9–16].

Strontium phosphates can form different phases in and from solutions. Some examples are α-[17, 18], β-[18, 19], and γ-SrHPO4 [20], Sr3(PO4)2·OH [21], and Sr3H2(PO4)3·2H2O [22]. Two primary methods, ex situ and in situ, can be used to understand the formation and transformation of these phases. In ex situ approaches, aliquots are removed during the reaction, centrifuged, washed, dried, and prepared for analysis. In addition to requiring a large number of samples and producing results with low temporal resolution, the steps necessary to prepare for ex situ analyses may cause changes in the crystal structure. Thus, the results might not reflect what actually occurs during the reaction [23]. In contrast, in situ characterisation methods are performed under real reaction conditions, which means that crystallisation processes may be monitored beginning with the early nucleation stages, through the rise of possible transient intermediates, and during product formation. This enables the development of rational synthesis protocols [24–34].

The in situ luminescence analysis of coordination sensors (ILACS) technique [35–37] uses the spectroscopic
sensitivity of lanthanide ions (Ln) to their coordination environment for monitoring chemical reactions. A specific example is the $5d \rightarrow 4f$ electronic transitions of Ln ions such as Eu$^{3+}$ and Ce$^{3+}$ [38–41], since the $5d$ orbitals are not shielded by outer orbitals. Therefore, the energy and position of the emission-peak maxima are sensitive to changes in the ligand field of these ions. The emission peaks assigned to $4f \rightarrow 4f$ electronic transitions of Ln ions such as Eu$^{3+}$ are not as prone to changes in the coordination environment. However, their narrow emission peaks allow better resolution of local symmetry and subtle ligand field effects, compared to broad $5d$–$4f$ emission bands [42].

To monitor crystallisation processes, these ions are introduced as local coordination sensors for the formation of a compound of interest. Changes in the coordination environment during nucleation, crystal growth, and phase transformations are detected under real reaction conditions using fast charge-coupled device (CCD)-based detectors. ILACS can be performed in conventional research laboratories and provides an efficient complementary approach for synchrotron-based in situ XRD analysis. This allows for the characterisation of ions in solution, and thus also desolvation processes.

In this work, we focus on the transformations between different strontium phosphate phases, especially those leading to the formation of SrHPO$_4$. To this end, we compared: 1) the crystallisation pathway suggested by ex situ analysis of aliquots removed during the reaction, 2) the pathway suggested by in situ measurements of Ce$^{3+}$ or Eu$^{3+}$-doped luminescence and light transmission, and 3) the pathway observed in synchrotron-based in situ X-ray diffraction analysis. With our findings, we aim to contribute to a better understanding of the crystallisation pathway of phosphates, enabling their rational synthesis and the improvement of their stability within technical and biomedical applications.

## 2 Results and discussion

To monitor the phenomena leading to the formation of SrHPO$_4$, Eu$^{3+}$ and Ce$^{3+}$ were chosen as coordination sensors, based on the sensitivity of their luminescence towards local structural changes in their coordinative environment. The crystallisation process of SrHPO$_4$ was monitored using real-time luminescence and synchrotron-based X-ray diffraction. Details of the reaction conditions are presented in the Experimental Section and in Table S1 in the Supplementary material (‡).

### 2.1 Eu$^{3+}$-doped strontium phosphates

Figure 1 summarises the preliminary results obtained during the synthesis of Eu$^{3+}$-doped SrHPO$_4$. As expected,
after starting the addition of Eu\textsuperscript{3+} and Sr\textsuperscript{2+}-containing solutions (exp. 1, Table S1\textsuperscript{3}), the intensity of the narrow bands (Figure 1a and S1\textsuperscript{1}) \( ^5\text{D}_0 \rightarrow ^7\text{F}_j \) \((j = 1, \lambda = 591 \text{ nm}; j = 2, \lambda = 614 \text{ nm}; j = 3, \lambda = 650 \text{ nm})\), representing the emissive transitions of Eu\textsuperscript{3+} rose and remained nearly constant (Figure 1a and b). The ratio of the integrated intensities of the \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) and \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) transitions is typically taken as a measure of the asymmetry of the coordinated sites occupied by the Eu\textsuperscript{3+} ions (Figure 1b) [42]. The suitability of this ratio as a semi-quantitative measure of structural changes is justified for the following reasons. The \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) transition has a strong magnetic dipole character. Because it is already parity-allowed, it is insensitive to the presence or absence of an inversion centre at the sites occupied by Eu\textsuperscript{3+} ions. In contrast, the \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition has a strong forced electric dipole character and gains intensity by odd-parity mixing (e.g. induced by the crystal field or vibrations) with wavefunctions of even parity, such as the 5d orbital, in accordance with the Judd–Ofelt theory [43,44].

As such, the transition is only very intense if the coordination environment of the Eu\textsuperscript{3+} ions is non-centrosymmetric [42]. In addition, the \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition is hypersensitive to local surroundings. Its intensity is affected by subtle changes in the surrounding ligand field in an unusually strong manner for intraconfigurational 4f–4f transitions [42]. Overall, any relative enhancement of the intensity of the emission peaks assigned to the \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition, compared to the relatively insensitive emission peaks due to the \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) transition, is a measure of the asymmetry of the coordination environment of the Eu\textsuperscript{3+} ions. This measure is referred to as the asymmetry factor \( R \) [42,45]. In experiment 1\textsuperscript{4}, the lowest values for \( R \) (Figure 1b, top panel) are reached at the beginning of the reaction. This result is expected due to the symmetric coordination environment of Eu\textsuperscript{3+} in aqueous solution [46] before reaction with the phosphate ions. Upon reaction with the phosphate anions offered in the solution, an increase in the \( R \) value was observed, which allowed monitoring of the desolvation process through an increase in the asymmetry around the Eu\textsuperscript{3+} ions. Interestingly, the \( R \) values increased until the Eu\textsuperscript{3+} and Sr\textsuperscript{2+} solution was completely added, with the growth rate changing approximately 9 min after the reaction started.

A similar behaviour was observed during monitoring of the time dependent growth rate of the intensity of the \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition (Figure 1b, purple curve), which becomes steeper at \( t \approx 9 \text{ min} \), before stabilising after 20 min. At this point in time, the addition of the Sr\textsuperscript{2+} and Eu\textsuperscript{3+} solution is stopped and the plateau indicates that the reaction reaches a steady-state.

Although the total emission intensity was relatively low, which resulted in a correspondingly low resolution of the different Eu\textsuperscript{3+}-related emission transitions, an additional change in the coordination environment could be recorded when the radiative \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) transition split into two peaks at 591 and 597 nm after approximately 9 min (Figure S1). The change in the splitting pattern of the respective emission peaks is indicative of a modification of the coordinative environment of the Eu\textsuperscript{3+} ions and leads to a lift in the degeneracy of the \( ^7\text{F}_1 \) spin–orbit level in the ligand field [42,47,48]. This is in agreement with the low symmetry of the coordinative environment, indicated by the asymmetry factor \( R = 1.8 \).

The reaction behaviour observed by the in situ luminescence spectra was confirmed by the simultaneously measured in situ X-ray diffraction analysis at the P23 beamline of the Deutsches Elektronen-Synchrotron (DESY) (Figure 1c). The evolution of Bragg reflections within the in situ XRD patterns is analogous to the observations in the luminescence spectra. Initially appearing and rising reflections can be assigned to the formation of the apatite phase Sr\(_5\)(PO\(_4\))\(_3\)OH (e.g. (002), (32; 1) and (300)) [21], which are subsequently substituted by the reflections assigned to \( γ\)SrHPO\(_4\) [20] (e.g. (210), (123), and (024); Figure 1c and Figure S2). These results are in agreement with the crystallisation behaviour of calcium phosphates, which is characterised by the transformation of Ca\(_5\)(PO\(_4\))\(_3\)OH to CaHPO\(_4\)-2H\(_2\)O during the reaction between the precursor compounds [13]. The evolution of the phases can be followed by the intensity of the reflections, which is shown in detail in Figure 1b (red and green curves) and is also compared to the in situ luminescence spectra. The reflections assigned to Sr\(_5\)(PO\(_4\))\(_3\)OH increased up to \( t \approx 14 \text{ min} \) at two different growth rates. The first growth rate lasted up to the 9 min point, which is in agreement with the initial increase in intensity of the Eu\textsuperscript{3+}-related \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition (Figure 1b, purple curve) and the evolution of the asymmetry factor \( R \) (Figure 1b, black dots). After approximately 14 min, the intensity of the Bragg reflections assigned to Sr\(_5\)(PO\(_4\))\(_3\)OH decreased (e.g. (32; 1), Figure 1b, red curve) and the intensity of the reflections assigned to \( γ\)SrHPO\(_4\) (e.g. (210), Figure 1b, green curve) started to increase. \( γ\)SrHPO\(_4\) continued to form until the end of the addition of the Sr and Eu precursors to the PO\(_4\)\(_3\)-containing solution (Figure 1b, blue curve). In this context, it is important to note that the decay of the normalised intensity \( I_{\text{norm}} \) of the reflection assigned to the Sr\(_5\)(PO\(_4\))\(_3\)OH phase (red curve, Figure 1b) and the increase in the intensity assigned to the \( γ\)SrHPO\(_4\) phase (green curve, Figure 1b) intersect at \( I_{\text{norm}} = 0.5 \). This suggests that the reaction mechanism more likely involves a solid-solid transformation, rather than a
partial dissolution of the $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ phase \cite{23, 49, 50}. After approximately 20 min, the intensities of the relevant Bragg reflections remain stable, which indicates that the reaction reaches equilibrium, similar to the results of the \textit{in situ} luminescence measurements. It is worth noting that the synchrotron radiation and the excitation light source did not significantly influence the reaction temperature. The temperature was kept constant at $(28.5 \pm 0.1) ^\circ \text{C}$ during the synthesis procedure (Fig. S3\textsuperscript{‡}).

\subsection*{2.2 Ce$^{3+}$-doped strontium phosphates}

Within the next set of experiments, we aimed to further understand the formation of $\text{SrHPO}_4$. To this end, Ce$^{3+}$, with a strong electric dipole-allowed $5d \rightarrow 4f$ transition located in the UV or visible range, was applied as a coordination sensor (exp. 2, Table S1\textsuperscript{‡}). Our previous studies on calcium phosphates have shown that the change of the coordination sensor from Eu$^{3+}$ to Ce$^{3+}$ does not influence the crystallisation behaviour of these materials \cite{13}. In the respective X-ray diffraction analysis performed at the P02.1 DESY beamline ($\lambda = 0.2073$ Å, Figure 2), the small angle range at $0.0$–$0.7^\circ 2\theta$ was measured simultaneously in the wide-angle range, $3.1$–$4.2^\circ 2\theta$.

Figure 2a shows a prominent increase in the background in the small angle range of the \textit{in situ} XRD patterns within the first 8 min of the chemical reaction, followed by a decrease. This behavior was not observed in the previous P23 \textit{in situ} XRD data due to the different detector position. This increase in the background is indicative of the formation of an X-ray amorphous phase \cite{13, 51}, in agreement with the formation of amorphous phases detected for other metal phosphates \cite{15, 52, 53}. The formation of this phase can also explain the increase in growth rate observed after the first 9 min of product formation, as detected in the \textit{in situ} luminescence spectra and XRD patterns of the corresponding solutions containing Eu$^{3+}$ (cf. Figure 1). The characteristic reflections assigned to $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ \cite{21} (e.g. (002), (32; $-0$) and (32; $-1$); Figure 2c and Fig. S3)

![Figure 2: a) and b) 3D \textit{in situ} XRD measurements recorded during the formation of $\gamma$-SrHPO$_4$;Ce$^{3+}$ at the P02.1 DESY beamline ($\lambda = 0.2073$ Å, exp. 2\textsuperscript{‡}). c) Comparison of \textit{in situ} XRD measurements with simulated XRD patterns for $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ \cite{21} (violet curve) and $\gamma$-SrHPO$_4$ \cite{20} (green curve). The blue and red curves highlight the single-phase transformation steps. d) Time dependence of the volume of $\text{Sr(NO}_3)_2$ and Ce(NO$_3$)$_3$·$\text{H}_2\text{O}$ to the reactor containing (NH$_4$)$_2\text{HPO}_4$ (blue curve). Comparison to time-dependence of the XRD intensity of the amorphous strontium phosphate (0.35$^\circ$ 2$\theta$, red curve), of the $\gamma$-SrHPO$_4$ phase (3.20$^\circ$ 2$\theta$, orange curve) and of the $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ phase (4.05$^\circ$ 2$\theta$, violet curve). The green curve displays the time dependence of the light transmission at 383 nm.](image-url)
increased within the first minute of the reaction, in a similar fashion to those of the Eu$^{3+}$-doped strontium phosphates. The intensities of the reflections assigned to this phase increased up to $t = 9$ min and then decreased.

Furthermore, the decrease in the concentration of the Sr$_5$(PO$_4$)$_3$OH phase coincides with the significant increase in the formation of $\gamma$-SrHPO$_4$ [20], detected through the rise of the characteristic reflections (e.g. (210), (123), (024), and (214); Figure 2c), which confirms the findings for the respective Eu$^{3+}$-containing strontium phosphates. The difference between the transformation of Sr$_5$(PO$_4$)$_3$OH to $\gamma$-SrHPO$_4$ at $t = 14$ min in experiment 1 and $t = 9$ min in experiment 2 is attributed to the slight change in the concentration in these experiments (Table S1$^\dagger$).

No significant changes in the concentration of the amorphous Sr$_5$(PO$_4$)$_3$OH or $\gamma$-SrHPO$_4$ phases were detected after the addition of Ce$^{3+}$ and Sr$^{2+}$ to the PO$_4$$^{3-}$-containing solution was completed (Figure 2d). It is noteworthy that the presence of the amorphous phase can still be registered after $t = 20$ min and its concentration only slowly decreases afterwards, accompanied by a simultaneous increase in the concentration of the $\gamma$-SrHPO$_4$ phase.

To investigate the impact of temperature on the phase transitions of strontium phosphates, the reaction temperature was raised to 80 °C after $t = 40$ min. This heating step caused a simultaneous increase in the intensity of the scattering peak of the amorphous phase and the observed Bragg reflections assigned to the $\gamma$-SrHPO$_4$ phase, which indicates an increase in the respective concentrations. The increasing intensity of the reflection at 4.05° 2θ, which is assigned to the Sr$_5$(PO$_4$)$_3$OH phase, is attributed to the overlap with a Bragg reflection at 4.10° 2θ assigned to $\gamma$-SrHPO$_4$.

In situ light transmission was measured simultaneously with in situ XRD analysis in Experiment 2$^\dagger$. During the addition of both Ce$^{3+}$ and Sr$^{2+}$ to the reactor, the light transmission at 383 nm increased up to $t = 9$ min, most probably due to the dilution of the PO$_4$$^{3-}$-containing solution by the cation solutions. Because the turbidity does not increase, the size of the formed amorphous and Sr$_5$(PO$_4$)$_3$OH particles clearly must be below the wavelength of the transmitted light [54]. After the formation of $\gamma$-SrHPO$_4$, an increase in turbidity was observed, which indicates an overall growth of the particle size. The turbidity was strongly reinforced by an increase in the reaction temperature after $t = 40$ min.

During experiment 3$^\dagger$, the same reaction conditions as in experiment 2$^\dagger$ were employed to perform in situ luminescence measurements ($\lambda_{ex} = 260$ nm) instead of in situ X-ray diffraction. Although the emission intensity reached the saturation limit of the detector during the experiments (Fig. S4$^\dagger$), exemplary measurements before ($t = 1$ min) and after ($t = 80$ min) saturation were used to acquire the emission spectra of Ce$^{3+}$-doped amorphous strontium phosphate, Sr$_5$(PO$_4$)$_3$OH, and $\gamma$-SrHPO$_4$.

At $t = 1$ min, after the addition of 2 mL of the Ce$^{3+}$- and Sr$^{2+}$-containing solution to the PO$_4$$^{3-}$-containing solution (Figure 3a, blue curve), a broad emission band covering a range between 300 and 500 nm was detected. This emission band, with a full width at half maximum (FWHM) of 4727 cm$^{-1}$, is composed of two overlapping main bands centred at 350 and 374 nm (Figure 3b, red curve). This double-band profile is typical for the Ce$^{3+}$-related $5d \rightarrow 4f$ electronic transition from the lowest excited $^2D_{3/2}$ level to the $^2F_{5/2}$ and $^2F_{7/2}$ ground levels, respectively [55]. The large FWHM is a result of inhomogeneous broadening due to the different crystallographic sites accommodated by the Ce$^{3+}$ ions in both phases. Energy dispersive X-ray (EDX) spectroscopy results indicated the presence of Ce$^{3+}$ in the final product (Fig. S6$^\dagger$).

![Figure 3](image-url)
At \( t = 80 \text{ min} \) (Figure 3b, green curve), the position of the Ce\(^{3+}\)-related emission band does not significantly differ from that measured at \( t = 1 \text{ min} \), and it still covers the same spectral range between 300 and 500 nm. The total FWHM increases to 5504 cm\(^{-1}\); this is attributed to the increase in temperature from 20.5 to 80.5 °C at \( t = 80 \text{ min} \) (Figure 3a). The product at \( t = 80 \text{ min} \) contained the amorphous phase and \( \gamma \)-SrHPO\(_4\), according to the corresponding in situ XRD analysis.

A similar wavelength range of the Ce\(^{3+}\)-based emission bands at both \( t = 1 \text{ min} \) and \( t = 80 \text{ min} \) is expected, because the average coordination environments of the Sr\(^{2+}\) sites substituted by Ce\(^{3+}\) do not differ significantly in Sr\(_5\)(PO\(_4\))\(_3\)OH and in \( \gamma \)-SrHPO\(_4\). In Sr\(_5\)(PO\(_4\))\(_3\)OH, two crystallographically independent Sr\(^{2+}\) sites are available: one is coordinated 7-fold and the other is coordinated 9-fold by oxygen atoms. The average Sr–O bond lengths are close to \( (2.7 \pm 0.1) \text{ Å} \) and \( (2.7 \pm 0.2) \text{ Å} \), respectively [21]. Similarly, two crystallographically independent Sr\(^{2+}\) sites are available in \( \gamma \)-SrHPO\(_4\), which are both ninefold coordinated by oxygen atoms with average Sr–O bond lengths of \( (2.7 \pm 0.1) \text{ Å} \) [20]. The presence of an OH\(^-\) ion in the coordination environment of hydroxyapatite, Sr\(_5\)(PO\(_4\))\(_3\)OH, instead of only phosphate-based oxygen atoms, leads to a chemically different ligand field. Moreover, PO\(_4\)\(^3-\) and OH\(^-\) ions differ in their optical basicities. Nonetheless, the presence of two Sr\(^{2+}\) sites, only one of which is coordinated by a single OH\(^-\) ion in the hydroxyapatite, and the very similar bond lengths in Sr\(_5\)(PO\(_4\))\(_3\)OH and \( \gamma \)-SrHPO\(_4\), lead to similar Ce\(^{3+}\)-based emission spectra (see Figure 3b). The broad-band nature of the emission of the Ce\(^{3+}\) ions does not allow sufficient distinction between these two phases, despite the generally higher sensitivity of 5\(d\)–4\(f\) transitions towards subtle coordinative changes. More advanced spectroscopic probes, such as luminescence decay experiments, are necessary to appropriately account for these changes. Thus, Eu\(^{3+}\) is a more suitable candidate for distinguishing the formation of Sr\(_5\)(PO\(_4\))\(_3\)OH from the formation of \( \gamma \)-SrHPO\(_4\) (see Figure 1b). Although the lack of long-range order in the amorphous phase does not allow for a consistent determination of any local coordinative structure by means of diffraction techniques, the similarity of the Ce\(^{3+}\)-related luminescence properties in all three phosphate phases shows that the coordination environment around the Ce\(^{3+}\) ions in the amorphous phosphate phase is similar to that in the Sr\(_5\)(PO\(_4\))\(_3\)OH and \( \gamma \)-SrHPO\(_4\) phases.

To demonstrate the relevance of in situ measurements for the elucidation of reaction events during the formation of strontium phosphates, an additional experiment was carried out. Experiment 4\(^*\) was performed under the same experimental conditions as experiments 2\(^*\) and 3\(^*\) (Table S1\(^*\)), but aliquots were removed from the reactor after selected time intervals. The colloidal solutions were quenched in a water bath at 2 °C, centrifuged, and the isolated solid residues were washed with H\(_2\)O and ethanol prior to drying at 80 °C for 2 h. The powders were analysed using ex situ XRD. In contrast to the in situ XRD measurements, the ex situ analyses indicated the formation of Sr\(_6\)H\(_3\)(PO\(_4\))\(_5\)·2H\(_2\)O after 5 min, while \( \beta \)-SrHPO\(_4\) was formed after 15 min (see Figure 4a). This difference is attributed to the preparation steps necessary for the ex situ analysis and the results no longer reflect the real-time phase transformations culminating in the formation of the \( \gamma \) polymorph.

The final product of experiment 4\(^*\), \( \beta \)-SrHPO\(_4\), was additionally analysed thermogravimetrically (TG) to characterise any thermally-induced phase transformations of...
the strontium phosphates (Fig. S7). The decomposition of \(\beta\)-SrHPO\(_4\) occurs in two main steps. The first one occurs at approximately 150 °C with the maximum differential thermogravimetric (DTG) signal at 384 °C, while the second one is observed between approximately 430 and 630 °C, with the maximum DTG at 587 °C. As shown in Figure 4b, the decomposition product of \(\beta\)-SrHPO\(_4\) after calcination at 700 °C is the expected condensed \(\beta\)-Sr\(_2\)P\(_2\)O\(_7\). This result is in agreement with previous findings on the thermal behaviour of CaHPO\(_4\) [56], which undergoes dehydration of its HPO\(_4^{2-}\) units with formation of \(\gamma\)-Ca\(_2\)P\(_2\)O\(_7\) after thermal treatment at 800 °C.

\(\beta\)-SrHPO\(_4\):Ce\(^{3+}\) shows a diffuse reflectance of almost 100% over the entire visible spectral range, in accordance with the colourless appearance of the powder under visible light irradiation (see Figure 5a). At wavelengths below 410 nm, the reflectivity decreases owing to the absorption of the Ce\(^{3+}\) ions. The emission spectrum of \(\beta\)-SrHPO\(_4\):Ce\(^{3+}\) is composed of two unresolved broad bands centred between 300 and 400 nm. The overall emission band has an FWHM of 4480 cm\(^{-1}\) (\(\lambda_{\text{ex}} = 260 \text{ nm}\), Figure 5b) and is assigned to the Ce\(^{3+}\)-related 5\(d\) → 4\(f\) electronic transition from the \(^4D_{3/2}\) level to the \(^2F_{5/2}\) and \(^2F_{7/2}\) ground levels, respectively [55]. The related excitation spectrum acquired by monitoring the emission at \(\lambda_{\text{em}} = 342 \text{ nm}\) (see Figure 5b) reveals the presence of several bands with maxima at 260 and 275 nm. These observations are in agreement with the luminescence properties reported by Wang et al. [6] Because there is a strong overlap between the absorption and emission of Ce\(^{3+}\) in \(\beta\)-SrHPO\(_4\):Ce\(^{3+}\) (see Figure 5a and b), self-absorption is expected, which favours energy transport and thus, concentration quenching at low concentrations.

It is noteworthy that the emission spectrum recorded for the \textit{ex situ} formed \(\beta\)-SrHPO\(_4\):Ce\(^{3+}\) (see Figure 5b) is slightly blue-shifted compared to those recorded for the mixtures of amorphous strontium phosphate, Sr\(_5\)(PO\(_4\))\(_3\)OH, and \(\gamma\)-SrHPO\(_4\) (Figure 3b). These findings indicate a slightly different coordinative environment of the Sr\(^{2+}\) ions in \(\beta\)-SrHPO\(_4\) with longer or shorter Ce–O bonds affecting the Ce\(^{3+}\) \(4f\) ground state, given that the Stokes shift is similar among the different phosphates.

### 3 Conclusions

The transformations between different strontium phosphate phases were monitored by combining \textit{in situ} and \textit{ex situ} measurements including (synchrotron-based) X-ray diffraction analysis, luminescence, light transmission, reflectance, and thermogravimetry. The \textit{in situ} techniques revealed the formation of an amorphous strontium phosphate and a hydroxyapatite (Sr\(_5\)(PO\(_4\))\(_3\)OH) phase upon mixing the respective precursor solutions, which ultimately led to the formation of \(\gamma\)-SrHPO\(_4\) (Scheme 1). In contrast, \textit{ex situ} XRD and luminescence characterisation of aliquots, which were removed at selected time intervals, indicated the presence of Sr\(_6\)H\(_3\)(PO\(_4\))\(_5\)·2H\(_2\)O and \(\beta\)-SrHPO\(_4\), which finally condensed to \(\beta\)-Sr\(_2\)P\(_2\)O\(_7\) above 700 °C (Scheme 1). These findings are in strong contrast to the phase composition of intermediates and products in solution, and demonstrate the importance of an appropriate \textit{in situ} characterisation of chemical reactions that are

![Scheme 1: Summary of strontium phosphate phases detected \textit{in situ} (amorphous strontium phosphate, Sr\(_5\)(PO\(_4\))\(_3\)OH, and \(\gamma\)-SrHPO\(_4\)), as well as \textit{ex situ} (Sr\(_6\)H\(_3\)(PO\(_4\))\(_5\)·2H\(_2\)O, \(\beta\)-SrHPO\(_4\), and \(\beta\)-Sr\(_2\)P\(_2\)O\(_7\)).](image)
prone to conflicting conclusions. The local coordination environments of Sr$^{2+}$ ions within amorphous strontium phosphate and β-SrHPO$_4$ were previously unknown. It was shown that the $4f^6 \rightarrow 4f^6$ luminescence of Eu$^{3+}$ is sensitive to changes in the coordination environment in aqueous solutions on the one hand and in various phosphate solids on the other. Ce$^{3+}$ was also chosen as the local coordination sensor. Given the premise that the Ce$^{3+}$ ions substitute the Sr$^{2+}$ ions within the phosphates, a comparison of the respective Ce$^{3+}$-related luminescence spectra provided additional insight into this topic. It can be concluded that the coordination environment of the Ce$^{3+}$ ions in doped amorphous strontium phosphate is similar to that in doped Sr$_2$(PO$_4$)$_3$OH and γ-SrHPO$_4$. In contrast, the coordination environment and Ce–O bond lengths in β-SrHPO$_4$ are expected to differ from those in Sr$_2$(PO$_4$)$_3$OH and γ-SrHPO$_4$. Thus, both in situ and ex situ luminescence studies with appropriate luminescent ions can be a valuable and simple tool to gain insights into local structural features, even without long-range crystalline order.

4 Materials

In a typical SrHPO$_4$ precipitation experiment, an aqueous solution containing Sr(NO$_3$)$_2$ (99%, Grüssing GmbH) and Eu(NO$_3$)$_3$·6H$_2$O (99.9%, ChemPur Feinchemikalien und Forschungsbedarf GmbH) or Ce(NO$_3$)$_3$·H$_2$O (99.5%, Alfa Aesar GmbH & Co KG) was added to the reactor containing an aqueous solution of (NH$_4$)$_2$HPO$_4$ (99%, Merck KGaA). Detailed descriptions of all solution concentrations and experimental conditions are summarised in Table S1.

After synthesis, the products were centrifuged, washed with water and ethanol, dried at 80 °C for 2 h, and subjected to ex situ analyses. Ex situ XRD measurements were performed in transmission geometry, applying a STOE Stadi-p X-ray powder diffractometer (STOE & Cie GmbH, Darmstadt, Germany) with a DECTRIS® MYTHEN 1 K detector (DECTRIS, Baden-Daettwil, Switzerland) using a Ge monochromator. Reflection spectra were recorded at room temperature with a Cary 5000 two-channel spectrometer (Varian Teclon Pty., Darmstadt, Germany) using BaSO$_4$ as a reference material. Thermogravimetric analysis was performed using a Linseis STA PT1600 simultaneous thermobalance; the samples were heated in a nitrogen atmosphere at a rate of 4 K min$^{-1}$.

4.1 Equipment for in situ measurements

The in situ experiments reported in this work were performed by applying two main experimental setups. The mobile Setup I was specifically designed to perform in situ XRD measurements at synchrotron facilities, while Setup II consisted of a stationary in situ crystallisation cell at the University of Kiel.

4.2 Setup I

To perform in situ X-ray diffraction analysis at synchrotron facilities, the glass reaction vessel was modified. The path length of the X-ray beam through the reaction volume was decreased by inserting a glass tube into one of its walls [36]. This vessel was placed in a reactor holder containing an integrated stirring system designed to flexibly fit different beamlines without requiring realignment after each reaction [13]. The reactor holder contains two openings for the entrance and exit of the X-ray beam. These are complemented by a larger opening for the irradiation of the reactor with the light source for in situ luminescence and light transmission measurements.

At the DESY P23 PETRA III beamline, in situ XRD measurements were carried out at 20 keV (λ = 0.6199 Å) using a Pilatus 1 M with an active area of 169 × 179 mm$^2$ and 172 × 172 µm pixel size as the X-ray detector (Figs. S8 and S9). X-ray diffractionograms were recorded at a time resolution of 1 s. The Shamrock 303i spectrograph coupled with a low-noise CCD IVAC camera (15 × 15 µm pixel size) was used for in situ studies of the luminescence properties. The spectrometer was connected to a sample cell using a quartz optical fibre. A fiber-coupled M375F2 LED (Thorlabs GmbH, wavelength 375 nm) was used as the excitation source.

At the DESY PO2.1 PETRA III beamline [57], in situ XRD measurements were carried out at 60 keV (λ = 0.2073 Å) using a Perkin Elmer XRD1621 detector (PerkinElmer Technologies, Walluf, Germany) (2048 × 2048 pixels, X pixel size 200.00 µm, Y pixel size 200.00 µm), and powder diffraction patterns were recorded every 30 s.

For the sake of clarity in the assignment of the in situ measured Bragg peaks to the respective simulated diffraction patterns, the XRD data was treated in the manner suggested by Platero-Prats et al. [58] for the in situ pair-distribution function measurements. Thus, our in situ XRD data was normalised to overcome the oscillation of the intensity of the synchrotron X-ray beam. We used the first measurement, prior to mixing the precursor solutions, as a baseline for subtracting the background caused by the reactor walls and the solvent.

In situ measurements of light transmission were performed by illuminating the reactor with a 395 nm light-emitting diode (LED, Sahlmann Photochemical Solutions, Germany). The intensity of the light source was measured during the reaction by an optical fibre submerged inside the solution and connected to a portable spectrometer (StellarNet Inc., Tampa, FL, USA) equipped with a CCD detector [59].

4.3 Setup II

This setup comprises an Easy MaxTM reactor system (Mettler Toledo GmbH, Gießen, Germany), capable of automatically controlling the temperature and stirring and dosing rates. The in situ luminescence measurements were performed using a Fluorolog-3 fluorescence spectrometer FL322 (HORIBA Jovin Yvon GmbH, Unterhaching, Germany), equipped with an IHR-320-FA triple grating imaging spectrograph, combined with a Syncerity CCD detector and a 450 W Xenon lamp. A Y-shaped optical fibre was used to transmit excitation light from the spectrometer to the solution and the light emitted from the reactor to the Syncerity CCD detector. In situ luminescence spectra were recorded every 30 s. Ex situ luminescence
spectra were detected using the R928P photomultiplier-based detector within the Fluorolog3 spectrometer.

Acknowledgments: Thanks go to the ILACS Group for the interesting discussions, M. Radke for the photos of the Setups and Dr. M. Köppen for the development of the in situ data helper software for analysing the DESY data. We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III P02.1 and P23 beamlines. Beamtime was allocated for proposals BAG-20170560 and II-20180600.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The authors thank Prof. Dr. W. Bensch for providing the equipment necessary for performing these experiments, as well as the German Research Foundation (DFG, Priority Program 1415 and project TE 1147/1-1) for financial support.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References


Supplementary Material: The online version of this article offers supplementary material (https://doi.org/10.1515/znb-2021-0182).