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Selective synthesis of *α*- and *β*-$SrHPO_4$ nanoparticles

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Abstract Nanoscale $SrHPO_4$ is prepared via a polyol-mediated synthesis. The resulting particles are well crystallized, non-agglomerated, and very uniform in size and shape. By adjusting the experimental conditions, $SrHPO_4$ can be obtained with the α-type as well as with the β-type of modification. In particular, particle diameters of 16 nm (α-$SrHPO_4$) and 12 nm (β-$SrHPO_4$) are obtained. The title compound is characterized by scanning electron microscopy, dynamic light scattering, X-ray powder diffraction, and infrared spectroscopy.

Introduction

$SrHPO_4$ has been claimed as a catalyst, proton conductor, and surface conditioner as well as for application in batteries, fuel cells, for flame proofing, and thermal cathodes [1–4]. Aiming at catalysis, the use of $SrHPO_4$ has been described for amination reactions, in particular, for its outstanding selectivity and conversion rate in the synthesis of diazabicyclo[2,2,2]octane [1]. Crystallograpically, $SrHPO_4$ has been described with three different types of modifications: α-$SrHPO_4$ is characterized by two crystallographically independent strontium sites—both with eightfold coordination to form a distorted quadratic antiprism [5]. Surprisingly, little is known with concern to β-$SrHPO_4$ as the thermodynamically most stable modification. Here, even sufficient single crystal structure data are still lacking. Finally, γ-$SrHPO_4$ has been reported to contain two independent Sr sites, which are both coordinated by nine oxygen atoms [6].

With concern to all applications mentioned above, a straight-forward access to nanoscale $SrHPO_4$ exhibiting non-agglomerated particles with high surface area can be of importance for fundamental as well as for applicational issues. Moreover, the question regarding crystallinity and type of modification of the as-prepared nanomaterial as well as the possibility to steer the type of modification arises. Surprisingly, the synthesis of nanoscale hydrogen phosphates as well as phosphates of the alkaline earth metals has been barely tackled, in general [7, 8]. In detail, $SrHPO_4$ has been realized via a water based coprecipitation [3, 9]. To this end, belt-type morphologies, 50–100 nm in widths and several microns in lengths as well as agglomerated mesoscaled particles, 150–200 nm in diameter have been obtained. In this study, the synthesis of highly crystalline and non-agglomerated $SrHPO_4$ with diameters below 50 nm is addressed. Furthermore, it is intended to steer the type of the crystallographic modification selectively by suited variation of the experimental conditions.

Experimental section

Synthesis

α-$SrHPO_4$ was prepared in a typical recipe by dissolving $Sr(NO_3)_2$ (151 mg/0.71 mmol, >99%, Riedel-de Haën) in 1 mL of deionised water and mixing with 50 mL of diethylene glycol (DEG) in a 1,000 mL beaker (solution A). In addition, H_3PO_4 (68 mg/0.69 mmol, >99.999%, Sigma Aldrich) was dissolved in 1 mL of H_2O and 5 mL of DEG (solution B). Solution A was heated to 170 °C and solution B rapidly added with vigorous stirring. By this measure an

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immediate particle nucleation was initiated. The resulting suspension was immediately quenched to 15 °C by addition of 150 mL of an ethanol/dry ice mixture. To separate the nanoparticles, the suspension was centrifuged (20 min, 26,000 rpm). The colorless nanomaterial was resuspended in and centrifuged from ethanol twice in order to remove all DEG and remaining salts. Finally, the powder was dried in a drying oven (15 min, 75 °C). The nanoscaled solid can be easily redispersed in DEG by sonification.

In a typical recipe for the polyol-mediated synthesis of nanoscale β-$SrHPO_4$, 50 mL of DEG (99%, Acros) were placed in a three-neck flask (volume 100 mL) with a Claisen stillhead. $Sr(NO_3)_2$ (150 mg/0.71 mmol, >99%, Riedel-de Haën) was dissolved in 1 mL of deionised water and added to DEG (solution A). In addition, H_3PO_4 (68 mg/0.69 mmol, >99.999%, Sigma Aldrich) was dissolved in 5 mL of DEG (solution B). The synthesis was performed under a continuous nitrogen flow. Solution A was heated to 90 °C to dissolve all starting materials and then cooled to 75 °C. For optimal conditions of nucleation and growth, solution B was rapidly added at this temperature under vigorous stirring. After 5 min of stirring, the suspension was rapidly heated (within 5 min) to 190 °C. Then the suspension was left to cool to room temperature and diluted with 50 mL of ethanol. Finally, the colorless nanomaterial was washed and dried as described above.

Analytical characterization

Dynamic light scattering (DLS) was conducted with polystyrene cuvettes applying a Nanosizer ZS (Malvern Instruments). Samples were measured after resuspension in DEG. Scanning electron microscopy (SEM) was carried out with a Zeiss Supra 40 VP, equipped with a field-emission gun (samples deposited on silicon and sputtered with Pt; acceleration voltage 10 kV; working distance 3 mm). X-ray powder diffraction (XRD) analysis was conducted with a Stoe Stadi P system, using Ge-monochromatized Cu-K_α radiation. Fourier-transform infrared (FT-IR) spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer; the samples were measured as pellets in KBr with a resolution of 4 cm^{-1}.

Results and discussion

To realize $SrHPO_4$ on the nanoscale, a polyol-mediated synthesis was applied. This type of synthesis has been widely used already to realize various nanomaterials, including elemental metals, oxides, sulfides or fluorides [10–12]. The background of synthesis, in general, is a multidentate and high-boiling alcohol (so-called polyol, e.g. diethylene glycol, ethylene glycol, glycerine) as the liquid phase. Due to the elevated temperature of synthesis (typically 150–300 °C) crystalline materials are often gained. The polyol furthermore coordinates, and therefore stabilizes the particle surface, which allows an efficient control of particle growth and agglomeration processes. Aiming at $SrHPO_4$, DEG was used as the polyol, $Sr(NO_3)_2$ and H_3PO_4 were selected as the starting materials. For optimal conditions of nucleation and growth [13], precipitation of the title compound was carried out by mixing homogeneous solutions of the starting materials.

With regard to the crystallographic modification—by means of thermodynamics—β-$SrHPO_4$ has been reported to represent the most stable modification at ambient conditions [5, 6]. Consequently, with increasing temperature and reaction time the formation of β-$SrHPO_4$ should be favored. On the other hand, the formation of a metastable modification is expected under kinetic control of the reaction. This expectation is consistent with findings for the bulk compound. According to Mooney et al. crystallization of α-$SrHPO_4$ has been observed as the initial product of chemical synthesis. Recrystallization of the thermodynamically stable β-form, thereafter is time-dependent and sometimes observed to occur spontaneously. In addition, transformation can be significantly fostered by increased temperatures [14, 15]. Analogous measures were evaluated here when aiming at nanoscale $SrHPO_4$. Indeed, α-$SrHPO_4$ was obtained according to the hot-injection method by mixing the starting materials at 170 °C. To suppress recrystallization, the suspension was immediately quenched by addition of an ethanol/dry ice mixture. Aiming at the β-modification, optimal conditions of nucleation mixing of the reactants were performed at moderate temperatures (75 °C). The resulting precipitate thereafter was crystallized by heating up to 190 °C. In accordance with Ostwald's step rule [16], the α-modification was preserved by quenching, but can be recrystallized by prolonged heating. X-ray diffraction patterns of both as-prepared nanomaterials indicate β-$SrHPO_4$ to be phase pure, and α-$SrHPO_4$ to contain only minor amounts of the β-phase (Fig. 1) [17, 18].

FT-IR spectroscopy was performed for further chemical characterization (Fig. 2). Spectra of α-$SrHPO_4$ and β-$SrHPO_4$ are almost identical, and also in accordance to those of bulk samples as published by Mel'nikova et al. [19]. To this end, the strong and broad band at 3,450 cm^{-1} is assigned to ν(O–H) [20]. Furthermore, three broad but weak bands between 3,000 and 1,500 cm^{-1} can be attributed to hydrogen bridge bonds. The manifold of sharp and partly splitted bands below 1,500 cm^{-1}, finally can be related to $\nu(PO_4)$, $\delta(PO_4)$ as well as to δ(O–H) vibrations. The number and splitting of these vibrational bands are in accordance with the low site symmetry (1) of the $[PO_4]^{3-}$ anion in the crystalline lattice [5].

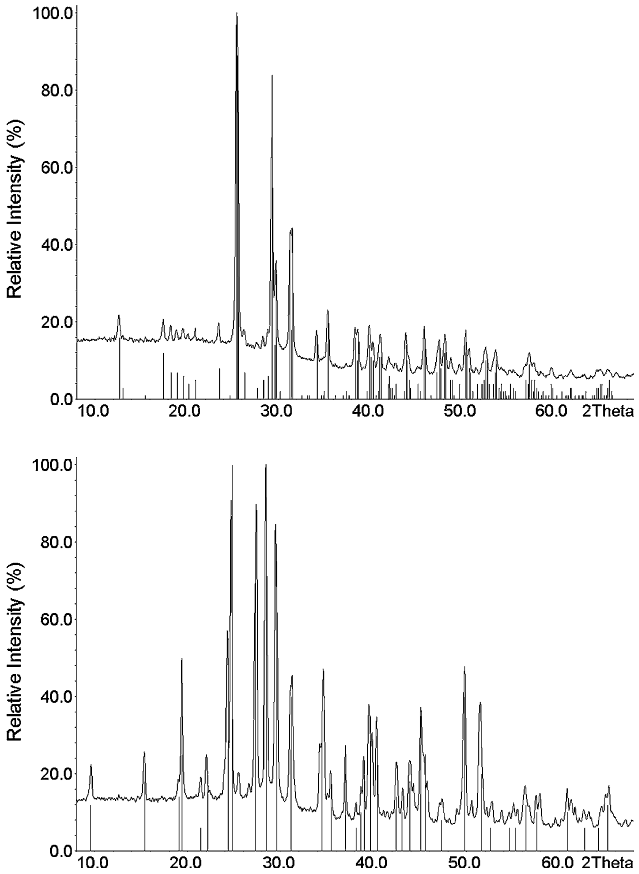

Fig. 1 XRD pattern of as-prepared α-$SrHPO_4$ (top, reference: ICDD-No. 01-070-1215) and β-$SrHPO_4$ (bottom, reference: ICDD-No. 012-0368)

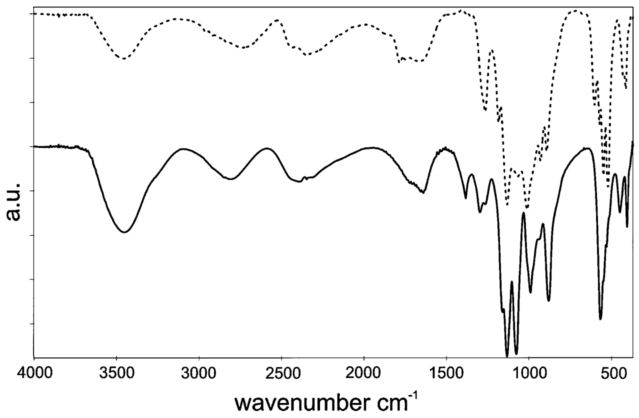

Fig. 2 FT-IR spectra of as-prepared α-$SrHPO_4$ (bold) and β-$SrHPO_4$ (dotted)

Particle size and size distribution of as-prepared α-$SrHPO_4$ and β-$SrHPO_4$ were verified based on electron microscopy (Fig. 3). Here, uniform particles with diameters of 16(3) nm (α-$SrHPO_4$) and 12(2) nm (β-$SrHPO_4$) are observed. These values were deduced based on a statistical evaluation of about 1,000 particles in each case.

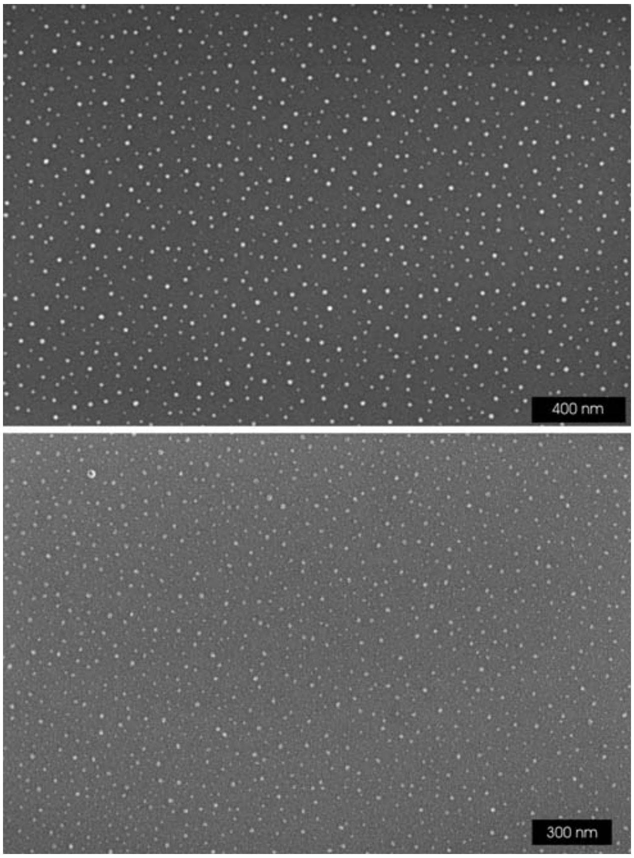

Fig. 3 SEM images of as-prepared α-$SrHPO_4$ (top) and β-$SrHPO_4$ (bottom)

In addition to powder samples, as-prepared suspensions in DEG were investigated with DLS measurements (Fig. 4). With the values of 13(2) nm (α-$SrHPO_4$) and 15(2) nm (β-$SrHPO_4$), the resulting hydrodynamic radii confirm the findings of electron microscopy. Moreover, the concurrence of particle diameters steming from SEM and DLS as well as the very narrow size distribution strike on the uniformity of the as-prepared nanomaterials and the absence of agglomerates.

Conclusions

Nanoscale $SrHPO_4$ was prepared via a polyol-mediated synthesis. By specific selection of the experimental conditions the title compound was yielded with two different crystallographic modifications. Based on a hot-injection of precursors and a rapid quenching of the resulting suspension, the formation of α-$SrHPO_4$ was initiated. While applying a continuous and slow heating process, the thermodynamically most stable β-$SrHPO_4$ was gained. According to the analytical characterization (XRD, FT-IR, SEM, DLS) both the as-prepared nanomaterials turned out to be highly crystalline, non-agglomerated, and very

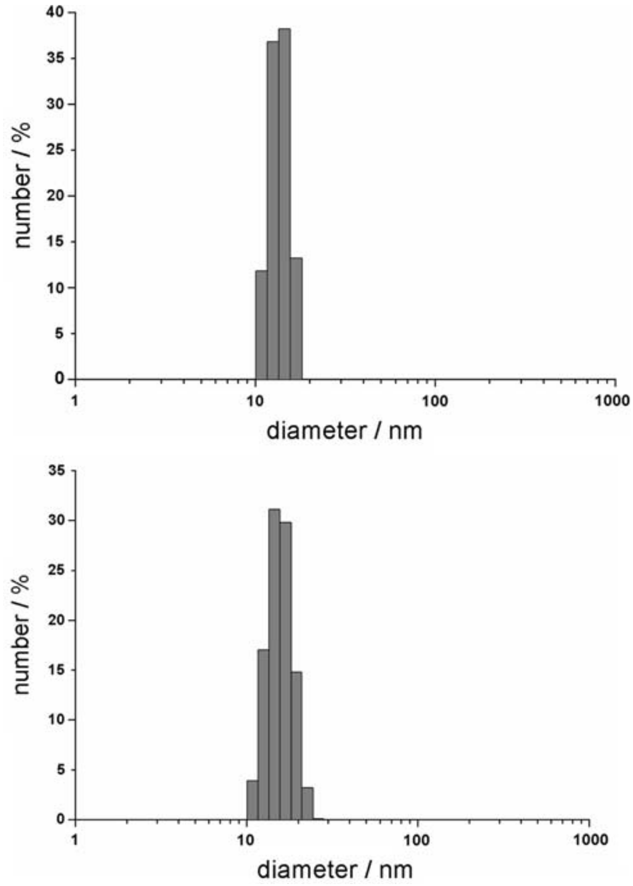

Fig. 4 Particle size distribution of as-prepared nanoscale α-$SrHPO_4$ (top) and β-$SrHPO_4$ (bottom) in DEG suspension

uniform in size and shape. In particular, particle diameters of 16 nm (α-$SrHPO_4$) and 12 nm (β-$SrHPO_4$) were obtained.

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