Direct synthesis and characterization of mixed-valent Li$_{0.5-x}$CoPO$_4$, a Li-deficient derivative of the Cmcm polymorph of LiCoPO$_4$†

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While the majority of research activities on LiCoPO$_4$ is focussed on the thermodynamically stable olivine-type Pnma polymorph, the metastable Pna$_2$$_1$ and Cmcm modifications have recently attracted considerable attention due to their interesting material properties. In this study, we present the first Li-deficient structural derivative of the Cmcm modification with the nominal composition Li$_{0.5-x}$CoPO$_4$. As opposed to the substoichiometric olivine (Pnma) phases Li$_x$CoPO$_4$ (x = 0; 2/3), which are exclusively accessible by electrochemical or chemical Li extraction techniques, this is also the first time that a direct soft-chemical synthesis route towards a Li$_x$CoPO$_4$-type material is accomplished. X-ray and neutron diffraction studies indicate that Cmcm-type Li$_{0.5-x}$CoPO$_4$ shows vacancies on both the Li and Co sites, whereas X-ray absorption spectra demonstrate that the structure features heterovalent Co ions (+2/+3) to compensate for the Li deficit. Magnetic measurements reveal a long-range antiferromagnetic order below 10.5 K. A thorough investigation of the thermal stability using thermogravimetric analysis, differential scanning calorimetry, and temperature-dependent in situ X-ray powder diffraction demonstrates that Li$_{0.5-x}$CoPO$_4$ is metastable and exhibits a complex, multi-step thermal decomposition mechanism. In the first step at 394 °C, it decomposes to α-Co$_2$P$_2$O$_7$ (P2$_1$/c) and LiCoPO$_4$ (Cmcm) upon O$_2$ release. The LiCoPO$_4$ (Cmcm) intermediate is then irreversibly transformed to olivine-type LiCoPO$_4$ (Pnma) at 686 °C. The material properties of Li$_{0.5-x}$CoPO$_4$ are further compared to the fully lithiated, isostructural LiCoPO$_4$ (Cmcm) phase, for which an improved structure solution as well as Co $L_{2,3}$-edge X-ray absorption spectra are reported for the first time.

Introduction

In the last two decades, thermodynamically stable, olivine-type (space group: Pnma) LiCoPO$_4$ polymorphs have been extensively studied as a high-voltage cathode material for lithium-ion batteries (operating voltage: ~4.8 V vs. Li/Li$^+$; theoretical capacity: 167 mA h g$^{-1}$).$^{1-4}$ The three-dimensional network structure features [CoO$_6$] octahedra, [PO$_4$] tetrahedra, and Li$^+$ ions in octahedral voids.$^5$ The majority of research activities have been focused on optimizing the electrochemical performance of the material.$^{6-8}$ However, despite intensive efforts, the nature of the intermediate phase Li$_x$CoPO$_4$, which occurs upon the two-step Li insertion–extraction reaction of LiCoPO$_4$, is still under investigation and debated in the literature. Earlier...
investigations suggested compositions of Li$_{0.7}$CoPO$_4$ (ref. 8) and Li$_{1.6}$CoPO$_4$*, respectively, whereas a later report stated a Li$_x$CoPO$_4$ ($x = 0.20–0.45$) composition. Recently, the lithiation state of the intermediate was determined to be Li$_{1.2}$CoPO$_4$ by two independent studies. Since the completely delithiated phase CoPO$_4$ is unstable and undergoes amorphization when exposed to air or moisture, the application of inert gas atmospheres and/or in situ techniques is crucial. According to Bramnik et al., both lithium-poor, Co$^{3+}$-containing phases are intrinsically unstable and exhibit a low thermal stability. Charged LiCoPO$_4$ electrodes were shown to decompose rapidly at temperatures below 200 °C, leading to gas evolution and the crystallization of Li$_2$CoPO$_4$ (only in the case of Li$_x$CoPO$_4$) and Co$_2$P$_2$O$_7$. In contrast, Theil et al. claimed that Li$_x$CoPO$_4$ is thermally stable up to 550 °C and that the thermal instability of charged LiCoPO$_4$ electrodes can be solely ascribed to the instability of the CoPO$_4$ phase. To the best of our knowledge, these Li-deficient phases are exclusively accessible by electrochemical or chemical Li extraction from LiCoPO$_4$ ($Pnma$) and a direct synthesis route has not been reported to date. Interestingly, in contrast to previous reports, we recently demonstrated that also the fully lithiated olivine-type LiCoPO$_4$ does not exhibit unlimited thermal stability since it transforms to the (at room temperature) metastable $Pnma$-$LiCoPO_4$ phase around 900 °C.

The less common, metastable LiCoPO$_4$ modifications, which crystallize in the space groups $Pnma$ (ref. 16, 18 and 19) and $Cmcm$, (ref. 16, 20 and 21) have recently attracted attention because of their interesting material properties and potential applicability as cathode materials for Li-ion batteries. The $Pnma$ modification exhibits a network of [PO$_4$] and [CO$_2$O$_4$] tetrahedra and Li$^+$ ions on tetrahedral sites. To date, the polymorph has only been accessible by microwave-assisted synthesis techniques. $Pnma$-type LiCoPO$_4$ shows the highest redox potential of $\sim$5.0 V vs. Li/Li$^+$ compared to the other two LiCoPO$_4$ polymorphs. A single redox peak was observed upon cycling, indicating that the compound is delithiated in one step. However, the electrochemical performance was found to be poor (maximum capacity: 33 mA h g$^{-1}$). Magnetic measurements indicated a paramagnetic Curie-Weiss-like behavior at high temperatures, and a long-range antiferromagnetic order below $T_N = 11$ K. Recently, a structure redetermination suggested that the material is non-stoichiometric and shows Li-Co anti-site defects, which provide an explanation for this poor performance.

A thorough investigation of the thermal stability revealed that LiCoPO$_4$ ($Pnma$) converts to the olivine LiCoPO$_4$ ($Pnma$) modification at 527 °C. Interestingly, the $Pnma$ structure re-emerges as a stable high-temperature phase above 800 °C.

The LiCoPO$_4$ ($Cmcm$) polymorph was first reported by Amaedor et al. using a high-pressure, high-temperature synthesis route (6 GPa, 900 °C). Alternative pathways using low-temperature procedures such as microwave-assisted solvothermal and polyol synthesis have been demonstrated recently. The structure is built from [CO$_2$O$_4$] and [PO$_4$] units, with Li$^+$ ions occupying tetrahedral sites. LiCoPO$_4$ ($Cmcm$) shows a single redox peak at $\sim$4.3 V vs. Li/Li$^+$ upon cycling, which corresponds to the lowest redox potential of all the LiCoPO$_4$ polymorphs. A discharge capacity of only 6 mA h g$^{-1}$ has been reported, which was associated with the poor conductivity of the material. The magnetic characterization suggested a long-range antiferromagnetic order below $T_N = 11$ K at low fields (10 kOe) and the presence of a metamagnetic transition.

Investigations on the thermal stability showed that the structure is metastable and transforms to olivine-type LiCoPO$_4$ ($Pnma$) at 575 °C, which then transforms to the $Pnma$ modification at 675 °C. The thermodynamically stable $Pnma$-LiCoPO$_4$ phase was obtained after cooling.

Based on our previous work on the three LiCoPO$_4$ polymorphs, we herein present the first Li-deficient structural derivative of the $Cmcm$ modification with the nominal composition Li$_{0.5}$-CoPO$_4$. To the best of our knowledge, this is the first time that a sub-stoichiometric LiCoPO$_4$ phase has been synthesized directly (bottom-up) by a soft-chemical poloyl approach as opposed to electrochemical or electrochemical Li extraction (top-down) techniques described in the literature. The structure, morphology, oxidation state as well as chemical and magnetic properties of the novel $Cmcm$-type phase Li$_{0.5}$-CoPO$_4$ are investigated. Moreover, the thermal properties are studied using thermogravimetry, differential scanning calorimetry, and temperature-dependent in situ X-ray powder diffraction. The results are discussed in context of the ‘fully lithiated’ LiCoPO$_4$ ($Cmcm$) phase, for which an improved structure solution (revealing a sub-stoichiometry reflected by the revised empirical formula Li$_{1-x}$CoPO$_4$) as well as X-ray absorption spectra are presented for the first time.

**Experimental**

**Synthesis of Li$_{0.5}$-CoPO$_4$ ($Cmcm$) and Li$_{1-x}$-CoPO$_4$ ($Cmcm$)**

$Cmcm$-type LiCoPO$_4$ samples with varied Li contents were obtained from a polyol process as described in our previous work using LiCH$_2$COO (ChemPur, 99+%), [Co(CH$_2$COO)$_2$$\cdot$4H$_2$O, Merck, 99.99%), and H$_2$PO$_4$ (Merck, 85 wt%) as precursors, and tetraethylene glycol (TTEG, Merck, $\approx$99.0%) as solvent. For the synthesis of Li$_{1-x}$-CoPO$_4$ ($Cmcm$), a Li:Co: P molar ratio of 3:1:10 was used, whereas Li$_{0.5}$-CoPO$_4$ ($Cmcm$) was obtained from a modified process using a ratio of 1:1:10. First, H$_3$PO$_4$ was added dropwise to a solution of cobalt acetate in 125 mL TTEG. Then, a second solution containing lithium acetate in 75 mL TTEG was added. The resulting mixture was refluxed at 185 °C for 14 h in a round-bottom flask. After cooling, the precipitate was recovered by centrifugation (1500 rpm, 20 min, three times) and washed with ethanol (VWR AnalaR NORMAPUR, 99.95%). The light pink powder (cf. graphical abstract) was collected by filtration, washed with acetone (99%), and dried in air at 100 °C for 14 h. Note that in contrast to the delithiated $Pnma$ structures Li$_x$CoPO$_4$ and in particular CoPO$_4$, which are sensitive to air and moisture, the $Cmcm$-derivative Li$_{0.5}$-CoPO$_4$ is stable under air for at least several months.

**X-ray powder diffraction (PXRD) and Rietveld refinement details**

Room-temperature PXRD data of the ground powders sealed in borosilicate glass capillaries (0.5 mm, Hilgenre) were
collected on a Stoe STADI P diffractometer (Mo $K_{\alpha}$ radiation, $\lambda = 0.70930$ Å; Ge(111) monochromator; Dectris MYTHEN DCS 1K silicon solid-state detector) in a 2$\theta$ range of 3–60° (PSD step: 0.015°; time per step: 30 s, three ranges, total measurement time: 12 h). The diffraction patterns were calibrated using an external silicon standard. The Jana2006 software$^{22}$ was used for the structure refinement by the Rietveld method, using the recently reported structure solution of LiCoPO$_4$ (Cmcm; ICSD no. 432186)$^{29}$ as a starting model. Details on the Rietveld refinement strategy and parameters used can be found in our previous work.$^{21}$

**Neutron powder diffraction (NPD) experiments**

Neutron powder diffraction data were collected using the diffractometer D2B at the Institut Laue-Langevin (ILL, Grenoble, France), working at a calibrated wavelength of 1.5942 Å in a 2$\theta$ range of 5–160°. The data were recorded at 296 K with a collection time of 4 h per pattern. The data were analyzed by the Rietveld method with the FULLPROF program.$^{21}$ The line shape of the diffraction peaks was generated by a pseudo-Voigt function. The instrumental contribution to the peak broadening was determined using an instrument resolution function built from the refinement of a Na$_2$Ca$_3$Al$_2$F$_6$ standard, while the wavelength was refined using a Si standard.

**Elemental analysis**

Analysis of the Li, Co, and P contents was carried out by atomic absorption spectroscopy (AAS, Varian AA280FS sequential device) and photometry (Shimadzu UV-160 photometer). A Hekatech Euro EA CHNSO combustion analyzer was used to determine the C, H, N, and S amounts.

**Soft X-ray absorption spectroscopy (soft XAS)**

Co $L_{2,3}$-edge soft XAS spectra were collected at beamline 8-2 of Stanford Synchrotron Radiation Lightsource (SSRL), operating the spherical grating monochromator (SGM, ruling: 1100 mm$^{-1}$) with 40 × 40 $\mu$m slits (resolution: ~0.3 eV), as described in our previous work.$^{17}$ The XAS spectra presented in this report are derived from the total electron yield (TEY), measured via the drain current (probing depth: 2–5 nm). We also recorded Auger electron yield (AEY) and total fluorescence yield (FY) spectra via a cylindrical mirror analyzer and a silicon diode (AXUV100). These modes, which probe ~2 nm and 50–100 nm deep, respectively, ensured that the best quality TEY spectra was bulk representative and that the contribution from surface contamination was small. All spectra were normalized to the incoming flux and the energy scale was calibrated to match that of ref. 24, followed by a background subtraction to a line, and a final area normalization for comparison. In order to produce the most stable and reproducible fits, the fitting was limited to the region just around the $L_3$ edge (774–784 eV), in which the normalization was further restricted through another line subtraction and area normalization.

**Fourier-transform infrared (FTIR) spectroscopy**

IR spectra were collected on a Varian 670 FTIR spectrometer equipped with a PIKE GladiATR diamond ATR stage. The measurements were performed using 132 scans in a wavenumber range of 400–4000 cm$^{-1}$.

**Magnetic measurements**

DC magnetization measurements were performed using a Quantum Design MPMS XL7 SQUID magnetometer in the temperature range from 2 K to 300 K with a magnetic field of up to 7 T. The powder samples were placed inside gelatin capsules. The temperature-dependent magnetic moments were recorded under an applied magnetic field of 1 kOe after cooling the samples under a magnetic field of 7 T (field-cooled, FC) and 0 T (zero field-cooled, ZFC). Magnetic hysteresis measurements were carried out with magnetic field strengths between −7 T and 7 T at 2 K, 11 K, and 300 K, respectively.

**Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)**

The stability of the material [specimen weight: ~10 mg] upon heating was assessed using a simultaneous Mettler Toledo TGA/DSC 1 STAR device, which did not allow to monitor the cooling cycle due to the setup. The measurement was run in a temperature range of 30–900 °C (heating rate: 10 °C min$^{-1}$) in an argon stream (10 mL min$^{-1}$), and additionally synthetic air (10 mL min$^{-1}$) in order to ensure comparability of the data with the in situ PXRD experiment.

**Temperature-dependent in situ X-ray powder diffraction (PXRD)**

Temperature-controlled PXRD was performed in situ under air using a PANalytical X'Pert Pro diffractometer (Bragg–Brentano geometry; Cu $K_{\alpha}$ radiation; Xcelerator detector) equipped with an Anton Parr HTK-1200 hot stage and a TCU 1000N temperature controller. The material was placed inside a corundum flat plate sample holder and heated up to 900 °C in steps of 100 °C (heating rate: 5 °C min$^{-1}$), with each temperature being held for 5 min before collecting the data. The scans were recorded in a 2$\theta$ range of 15–70° (step: 0.022°; time per step: 209.5 s; total experiment time: 145.5 h).

**Results and discussion**

**Rietveld refinement of X-ray and neutron powder diffraction data**

Fig. 1a shows the Rietveld fit of the X-ray powder diffraction pattern of the as-prepared title compound Li$_{0.5}$CoPO$_4$. The pattern of a reproduced sample of Cmcm-type LiCoPO$_4$ (Fig. 1b) is in good agreement with our previous work.$^{21}$ In both cases, all the reflections can be indexed in the orthorhombic space group Cmcm and no additional reflections are observed, indicating that both materials are phase pure. While the pattern of Li$_{0.5}$CoPO$_4$ appears to be roughly similar to the one of LiCoPO$_4$, suggesting that the crystal structure of the Li-deficient
compound is strongly correlated with the one of the fully lithiated material, some shifts in the peak positions can be recognized. The most significant feature of the Li$_{0.5}$Co$_{0.5}$PO$_4$ pattern is the narrowing of the (200) and (112) reflections at 15.0° and 15.9° 2θ. Furthermore, a completely different peak pattern can be observed in the 2θ region of 25.5–27.5° (for a detailed view, please refer to Fig. S1, ESI†).

To gain further insights into the structural differences causing the peak shifts, a Rietveld refinement was performed, using the previously published structure solution of Cmcm-type LiCoPO$_4$ (ICSD no. 143186) as a starting model. Since the elemental analysis indicated an approximate 50% deficit in Li for Li$_{0.5}$Co$_{0.5}$PO$_4$ compared to Cmcm-LiCoPO$_4$ (cf. Table 2) within standard deviations, the structures were at first refined with fixed Li site occupancy factors of 50% and 100%, respectively, resulting in good reliability factors (Table S1, ESI†). Taking into account that the empirical formulas derived from elemental analysis indicated a deficit in both Li and Co for the two materials (empirical formulas: Li$_{0.45(5)}$Co$_{0.93(5)}$P$_{1.00(2)}$O$_4$ and Li$_{0.93(3)}$Co$_{0.91(3)}$P$_{1.00(2)}$O$_4$; cf. Table 2), we tentatively refined the occupancy factors of the Li and Co sites after having applied an absorption correction. In both cases, the free refinement resulted in statistically significant values for the occupancies (39(2)% Li and 96.4(5)% Co for Li$_{0.5}$Co$_{0.5}$PO$_4$; δ = 0.11(2) and 94(2)% Li and 95.5(5)% Co for LiCoPO$_4$; cf. Table S2, ESI†), indicating that both structures feature vacancies in the cationic substructures and are non-stoichiometric. In both cases, the reliability factors were significantly improved over the previous structure models with fixed occupancies (cf. Tables 1 and S1, ESI†). To simplify the sum formulas of both compounds while still reflecting the off-stoichiometry from the idealized formulas Li$_{0.5}$Co$_{0.5}$PO$_4$ and LiCoPO$_4$ (within three standard deviations), the compounds are referred to as Li$_{0.5}$Co$_{0.5}$PO$_4$ for the Li-deficient phase, and Li$_{0.9}$CoPO$_4$ (with γ = 0.06(2)) for Cmcm-type LiCoPO$_4$ in this work. It is worth noting that on basis of these refinements, there was no indication for the occurrence of antisite defects, which are profound for materials synthesized at low temperatures (as observed e.g. in Ptn2$_1$-type LiCoPO$_4$).

Furthermore, in contrast to Li$_{0.94(2)}$Co$_{0.96(1)}$PO$_4$, the composition of the Li-deficient Cmcm derivative Li$_{0.39(2)}$Co$_{0.96(1)}$PO$_4$ would not be charge-balanced assuming that Co is only present in the oxidation state +2. We therefore assume that the deficit in positive electric charge caused by the lower Li$^+$ content is compensated by Co$^{3+}$ in the framework, which was confirmed by X-ray absorption spectroscopic studies discussed later.

The refined cell parameters (Table 1) indicate a significant contraction along the a axis and an expansion along the c axis for Li$_{0.5}$Co$_{0.5}$PO$_4$ compared to Li$_{0.9}$CoPO$_4$, while b is not significantly changed, hence providing an explanation for the peak shifts observed in the PXRD patterns. Furthermore, the respective cell volumes (V = 278.116(19) Å$^3$ vs. 276.28(2) Å$^3$, corresponding to an increase of 0.7%) reveal that the Li$_{0.5}$Co$_{0.5}$PO$_4$ structure is less dense, which is consistent with the decrease in crystal densities. This is surprising since for the delithiated phases Li$_0$CoPO$_4$ and CoPO$_4$ derived from olivine-

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Table 1  Crystallographic parameters of (a) Li$_{0.5}$CoPO$_4$ in comparison with (b) Li$_{0.9}$CoPO$_4$ (both Cmcm, Z = 4) as refined from X-ray powder diffraction data (T = 298 K)$^a$

| Sample | Li$_{0.5}$CoPO$_4$ | Li$_{0.9}$CoPO$_4$ |
|--------|-----------------|------------------|
| Empirical formula | Li$_{0.45(5)}$Co$_{0.93(5)}$P$_{1.00(2)}$O$_4$ | Li$_{0.94(2)}$Co$_{0.96(1)}$PO$_4$ |
| M$_f$ (g mol$^{-1}$) | 154.3 | 158.1 |
| Space group (no.) | Cmcm (63) | Cmcm (63) |
| Crystal system | Orthorhombic | Orthorhombic |
| Z | 4 | 4 |
| a (Å) | 5.338(5) | 5.443(3) |
| b (Å) | 8.176(3) | 8.165(4) |
| c (Å) | 6.3176(2) | 6.2128(3) |
| V (Å$^3$) | 278.116(19) | 276.28(2) |
| F(000) | 297 | 302 |
| ρ (calcd) (g cm$^{-3}$) | 3.684(1) | 3.800(1) |
| R$_p$ | 0.0257 | 0.0196 |
| R$_wp$ | 0.0327 | 0.0255 |
| R$_exp$ | 0.0267 | 0.0252 |
| R$_f$ | 0.0143 | 0.0106 |
| R$_B$ | 0.0254 | 0.0184 |
| χ$^2$ | 1.23 | 1.01 |
| Data/restraints/parameter | 3800/0/59 | 3835/0/57 |

$^a$ The estimated standard deviations were calculated by the Berar’s procedure and are indicated in parentheses.

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type LiCoPO₄ (Pnma), a significant decrease in cell volume of up to ~7% (CoPO₄) was observed due to the smaller ionic radius of Co³⁺ compared to Co²⁺. The slight increase in cell volume might be explained by the fact that our Li-poor Cmcm material was produced from a kinetically controlled synthesis as opposed to Pnma-type CoPO₄, which was obtained by electrochemical Li extraction. As a result, the Li ions and voids are likely to be statistically distributed within the Cmcm structure. This structure is in good agreement with the X-ray data. The refinement of the site occupancy factors revealed 37(4)% Li and 98(2)% Co for Li₀.₅₋₀.₆CoPO₄ (δ = 0.13(4)), and 90(3)% Li and 95(6)% Co for Li₁₋₀.₇CoPO₄ (γ = 0.10(3)) (Table S5, ESI†). The compositions and structural parameters of Li₀.₃₇(4)Co₀.₉₈(1)PO₄ and Li₀.₉₀(2)Co₃⁺(6)PO₄ are very close to the ones derived from the X-ray experiment and hence confirm the structure model.

Crystal structure

The structures of both Cmcm-type LiCoPO₄ materials feature rows of edge-sharing, distorted [CoO₆] octahedra which are running along the [001] direction as illustrated in Fig. 2a. The [CoO₆] rows are cross-linked along [100] by alternating pairs of edge-sharing, asymmetric [PO₄] and [LiO₄] units (note that the tetrahedrally coordinated Li ions are shown in Fig. 2 instead of [LiO₄] tetrahedra for clarity). As a result, layers of the composition ([CoO₆][LiO₄][PO₄]) are formed in the ac plane (Fig. 2b). In these layers, every [CoO₆] octahedron shares two opposite O2–O2 edges with neighboring [CoO₆] units, and two apical O2 atoms with two different [PO₄] and [LiO₄] tetrahedra, which connect the [CoO₆] strands (for details see Fig. S3, ESI†). The layers are in turn stacked in the sequence AB (indicated by black and grey boxes in Fig. 2a and c) along [010] with a displacement of a/2 via the apical O1 atoms of the [CoO₆] units so that a three-dimensional framework is formed. It has to be emphasized that despite the fact that Li channels seem to occur along [100] (Fig. 2a), the Li–Li distances are very large (d = 5.3385(4) Å and 5.4432(5) Å, cf. Table S2b and d, ESI†), so that these sites are considered isolated. Hence, Li migration will require a very high activation energy along this path and the Li mobility is extremely low in both structures. The lack of suitable Li migration pathways is confirmed by electrochemical measurements (see Section 5 and Fig. S4, ESI†) that revealed a very poor performance for both Cmcm materials (discharge capacities of < 3 mA h g⁻¹), and is also in line with a previous report. Hence, due to the intrinsically low Li-ion conductivity, the Li₀.₅₋₀.₆CoPO₄ and Li₁₋₀.₇CoPO₄ phases cannot be considered suitable for battery applications.
The structural differences between Li$_{1-x}$CoPO$_4$ and its Li-deficient analogue Li$_{0.5-x}$CoPO$_4$ can be derived from the cell parameters (Table 1) and the interatomic distances (Table S3b and d, ESI†). In general, the framework of Li$_{0.5-x}$CoPO$_4$ is contracted by ~0.10 Å in the a dimension and expanded by ~0.01 Å along c and b, respectively, as also indicated by the distances between the Co centers in and between the layers. The average Co–O (2.122 Å in Li$_{0.5-x}$CoPO$_4$ vs. 2.123 Å in LiCoPO$_4$) and P–O (1.539 Å vs. 1.538 Å) distances in the [CoO$_6$] and [PO$_4$] units remain virtually unchanged, which is surprising since one would expect a decrease in the Co–O distances due to the occurrence of a definite amount of the smaller Co$^{3+}$ ion compared to Co$^{2+}$ in the structure. The individual bond lengths, however, reveal that both the [CoO$_6$] and [PO$_4$] units show a higher degree of distortion. This is reflected by the fact that the Co–O2 and P–O2 distances (in the [CoO$_6$] and [PO$_4$] layers) are shortened, whereas the Co–O1 and P–O1 bonds (connecting the layers along b) are expanded, resulting in an increase of the distance between the A–B layers (cf. Co–P distances). On the other hand, the mean Li–O distances are increased by ~0.4 Å, leading to an expansion of the channels along [100]. This is consistent with the increase of the Li–Li distances by ~0.10 Å. However, it has to be noted that we cannot provide any information about the ordering of the Li$^+$, Co$^{2+}$, and Co$^{3+}$ ions or the vacancies in the structure. Based on considerations on the charge distribution, it is likely that the vacancies in the Li$_{0.5-x}$CoPO$_4$ framework are located next to the Co$^{3+}$ centers, which would be consistent with DFT (density functional theory) studies on the Li$^+$/vacancy distribution in olivine-type Li$_{2/3}$CoPO$_4$.

Elemental analysis

The results of the elemental analysis of Li$_{0.5-x}$CoPO$_4$ (Cmcm) are compared to the values of Cmcm-type LiCoPO$_4$ from our recent report on the Cahn–H有幸–Nold (CHNS) analyses are similar and show small amounts of hydrogen and carbon in both materials, which arise from residual tetraethylene glycol (TTEG) solvent or the decomposition products of TTEG and the acetate precursors and contents found in the obtained materials are not correlated linearly. Adjusting the molar ratio of the precursors might therefore provide a synthetic strategy towards other lithium cobalt or transition metal phosphate materials with modified Li contents. Given the fact that the delithiated Pnma phases Li$_{2/3}$CoPO$_4$ and CoPO$_4$ are only accessible by chemical or electrochemical Li extraction from the fully lithiated olivine-type LiCoPO$_4$ (Pnma) material and very instable, this bottom-up approach might also pave the way towards the direct and simple soft-chemical preparation of these Li-deficient intermediates. In that matter, the influence of the synthesis route on the chemical composition will have to be thoroughly examined in further experiments.

X-ray absorption spectroscopy

L$_{2,3}$-edge X-ray absorption spectroscopy is highly sensitive to the oxidation state as well as the spin state and chemical environment of transition metals. We have therefore applied Co L$_{2,3}$-edge XAS to investigate the chemical state (valency and symmetry) of the cobalt ions in Li$_{0.5-x}$CoPO$_4$ (Cmcm) and Li$_{1-x}$CoPO$_4$ (Cmcm). Fig. 3 displays the normalized TEY spectra over the L$_{3}$-edge region from this study along with reference
spin (HS) Co\(^{2+}\) as well as both low-spin (LS) and high-spin (HS) octahedral crystal. The Co\(^{3+}\) association and the lower energy shoulder of Co\(^{3+}\) (779.4 eV) results in a near identical spectral weight are apparent (see text). All datasets have been aligned to match the common energy scale of ref. 24. The vertical dashed lines indicate the energies corresponding to Oh Co\(^{2+}\) (776.4 eV) and Oh Co\(^{3+}\) (779.4 eV).

Fig. 3 Normalized Co L-edge XAS spectra in the TEY mode for (a) Li\(_{0.5}\)CoPO\(_{4}\) (Cmcm, blue), (b) Li\(_{1}\)CoPO\(_{4}\) (Cmcm, red) along with reference spectra for (c) Oh, high-spin Co\(^{2+}\) in CoO (adapted from ref. 24, black), and (d) low- and (e) high-spin Co\(^{3+}\) in EuCoO\(_3\) and Sr\(_2\)CoO\(_4\)Cl (from ref. 30, both black). (f) shows the difference spectrum resulting from a subtraction of 71% Co\(^{2+}\) from Li\(_{0.5}\)CoPO\(_{4}\) (orange), Li\(_{1}\)CoPO\(_{4}\) (subtraction), representing the trivalent Co\(^{3+}\) ion in the compound. The Co\(^{3+}\) association and the lower energy shoulder spectral weight are apparent (see text). All datasets have been aligned to match the common energy scale of ref. 24. The vertical dashed lines indicate the energies corresponding to Oh Co\(^{2+}\) (776.4 eV) and Oh Co\(^{3+}\) (779.4 eV).

Charge balance arguments suggest that Li\(_{0.5}\)CoPO\(_{4}\) (Cmcm) bears cobalt ions in nominal oxidation states of both +2 and +3. Fitting of the spectrum using principal Co\(^{2+}\) and Co\(^{3+}\) components results in relative contributions of approximately (71 ± 3)% Co\(^{2+}\) and (29 ± 3)% Co\(^{3+}\) (as opposed to (97 ± 3)% Co\(^{2+}\) and (3 ± 3)% Co\(^{3+}\) for Li\(_{1}\)CoPO\(_{4}\)), where the symmetry and spin state of the trivalent Co has some, but not dominating effects on the distribution. These values are in line with the Co\(^{2+}\) and Co\(^{3+}\) contents expected on basis of the nominal composition Li\(_{0.5}\)CoPO\(_{4}\) (~50% Co\(^{2+}\) and ~50% Co\(^{3+}\)), but where the Co\(^{3+}\) contribution derived from XAS is lower. The discrepancy can partly be explained by a small but noticeable reduction at the surface, in line with the fact that Co\(^{3+}\) is significantly less stable than Co\(^{2+}\). Moreover, the material was produced using a TTEG solvent, which also acts as a weak reducing agent\(^{24,29}\) and hence, might reduce the Co\(^{3+}\) concentration on the particle surface (cf. probing depth of TEY: 2–5 nm). We note that the more bulk sensitive spectra (FY, not shown) indicated higher spectral weight towards higher energies (and thus more Co\(^{3+}\) in the bulk), consistent with this hypothesis, but the spectra are not of high enough quality to be analyzed or discussed further.

In order to learn more about the symmetry and spin of the Co\(^{3+}\) sites, we have subtracted the fitted Co\(^{2+}\) contribution from the Li\(_{0.5}\)CoPO\(_{4}\) spectrum (Fig. 3f). We note that while the main intensity difference is centered around the energy associated with the main peak of Co\(^{3+}\) (779.4 eV), there is significant intensity on the low-energy side of this peak that is not accounted for by the LS Co\(^{3+}\). Comparison with Co\(^{3+}\) ref. 30 of different spin indicates that the trivalent Co ions are primarily high-spin, which can be rationalized based on the tetragonal distortions in the [CoO\(_6\)] octahedra (cf. Table S3, ESIF) and the analogous HS Co\(^{3+}\) L-edge spectral assignment upon axial elongations and equatorial contractions in various perovskites\(^{10,31,14}\). The XAS thus indicates that the Li vacancies are indeed inducing distortions near the Co\(^{3+}\) sites that favor the HS Co\(^{3+}\) state. The HS Co\(^{3+}\) state is also consistent with a larger average Co–O distance (i.e., larger ionic radius) than what would be expected from the (smaller) LS Co\(^{3+}\) that only occupies the t\(_{2g}\) orbitals and is associated with a stronger, more covalent Co–O interaction (cf. Table S3, ESIF). The presence of HS Co\(^{3+}\) is further consistent with the large magnetic moment (see later).

Fig. 4 Comparison of the FTIR spectra of (a) Li\(_{0.5}\)CoPO\(_{4}\) (Cmcm, blue), and (b) Li\(_{1}\)CoPO\(_{4}\) (Cmcm, red, data reproduced from ref. 21). The omitted region of 1700–4000 cm\(^{-1\)} (cf. Fig. S6, ESIF) does not show any absorption bands of water or other impurities.
Infrared spectroscopy

Fig. 4 compares the infrared spectra of Li_{0.5–x}CoPO_{4} (Cmcm) and Li_{1–x}CoPO_{4} (Cmcm; data reproduced from ref. 21) in the range of 400–1700 cm\(^{-1}\). The omitted region from 1700 cm\(^{-1}\) to 4000 cm\(^{-1}\) is presented in Fig. S6 (ESI†) and does not show any absorption bands of water or other impurities. As expected, both spectra are dominated by the four fundamental vibrations of the pseudo-tetrahedral phosphate groups. Two regions can be distinguished, with the symmetric (\(v_1\)) and asymmetric (\(v_4\)) stretching vibrations of P–O being observed at higher frequencies, as well as the symmetric (\(v_2\)) and asymmetric (\(v_4\)) bending vibrations of the O–P–O group at lower frequencies. According to previous reports, due to the additional absorption band at 1512 cm\(^{-1}\) (Fig. 4a) shows some distinct differences, in particular a shift of the band frequencies to slightly lower energies and band broadening, and the appearance of additional weak bands at 1512 cm\(^{-1}\) and 1138 cm\(^{-1}\).

The changes observed for the Li-deficient phase Li_{0.5–x}CoPO_{4} are in line with reports on olivine-type LiFePO_{4} (0 ≤ x ≤ 1) which demonstrated that the absorption modes of the [PO\(_4\)]\(^{3–}\) groups are extremely sensitive to the delithiation of LiFePO_{4} and the associated oxidation of Fe\(^{2+}\) to Fe\(^{3+}\). As discussed, the average P–O distances in Li_{1–x}CoPO_{4} (Cmcm) remain virtually unchanged when less Li is incorporated in the structure (cf. Table S3, ESI†). Hence, the energies of the absorption modes are not changed drastically, indicating similar local structures of the [PO\(_4\)]\(^{3–}\) units. This is in good agreement with a report by Popović and co-workers, which suggested a linear correlation between the P–O bond lengths and stretching frequencies. The observed band splitting, on the other hand, is correlated with interactions between ions, in this case between the [PO\(_4\)]\(^{3–}\) units and the adjacent Li\(^{+}\) and Co\(^{2+/3+}\) cations, i.e. the stronger the interaction, the larger the factor group splitting effects. In fact, the P–Li and P–Co distances are reduced in Li_{0.5–x}CoPO\(_4\) compared to Li_{1–x}CoPO_{4} (Table S3, ESI†), which leads to stronger interactions. Furthermore, it was shown that the factor group splitting of the \(v_3\) modes increases with the second ionization potential of the transition metal due to the formation of strong bonds with the oxygen atoms of the [PO\(_4\)]\(^{3–}\) units, which causes a redistribution of electron density in the P–O bonds. This is reflected in the observation that the P–O1 bonds are expanded, and the P–O2 bonds shortened by ~0.02 Å each in Li_{0.5–x}CoPO_{4} (cf. Table S3, ESI†). Due to the significantly higher ionization potential of Co\(^{3+}\) compared to Co\(^{2+}\), the larger factor group splitting in the IR spectrum of Li_{0.5–x}CoPO_{4} is therefore the result of the mixed valence state of the Co ion in the structure (Co\(^{3+}/Co^{3+}\)) as opposed to Li_{1–x}CoPO_{4} which contains Co\(^{2+}\) only. However, a thorough analysis of the spectra, including the assignment of the additional absorption band at 1512 cm\(^{-1}\), would require a complete structural model, including the ordering of the Li\(^{+}\), Co\(^{2+}\), and Co\(^{3+}\) ions in the framework as well as DFT calculations, which is beyond the scope of this work. It is likely that the occurrence of additional modes is the result of a lower local symmetry in Li_{0.5–x}CoPO_{4} due to a higher defect concentration.

Magnetic properties

Fig. 5 shows the magnetic susceptibility as function of temperature measured at a magnetic field of 0.1 T in field-cooled (FC) condition as well as the magnetic hysteresis recorded at a temperature of 2 K of Li_{0.5–x}CoPO_{4} in comparison with Li_{1–x}CoPO_{4} (both Cmcm). The temperature dependence of the magnetic susceptibilities indicates a long-range antiferromagnetic to paramagnetic transition at \(T_N = 10.5\) K for Li_{0.5–x}CoPO\(_4\) and \(T_N = 12\) K for Li_{1–x}CoPO\(_4\) respectively. The low transition temperature \(T_N\) of 12 K of the Li_{1–x}CoPO\(_4\) phase is in agreement with our previous study on olivine-type LiCoPO_{4} and is comparable to the non-olivine, metastable LiCoPO_{4} (Pna2\(_1\)) phase (\(T_N = 11\) K), but much lower than the well investigated olivine-type LiCoPO\(_4\) (Pnma, \(T_N = 21.6\) K). This finding demonstrates the close relation between structural and magnetic properties. However, the further reduction of the observed transition temperature \(T_N\) of the Li-deficient Li_{0.5–x}CoPO\(_4\) compound might be related to the vacancies on the Co site, weakening the Co–O–Co super exchange interaction. Above the transition temperature, the magnetic susceptibility of both compounds follow the Curie-Weiss law (see Fig. S7, ESI†). A temperature-independent contribution, \(\mu_{\text{eff}}\), the effective magnetic moment, \(N_A\), the Avogadro number, \(\theta_C\), the Weiss temperature, and \(k_B\), the Boltzmann constant. Fitting the high-temperature magnetic susceptibility with the Curie-Weiss law yields a higher Weiss temperature of ~21.8 K of Li_{0.5–x}CoPO_{4} compared to the stoichiometric Li_{1–x}CoPO_{4} (~28.2 K; cf. inset of Fig. S7, ESI†), which reflects the difference in transition
temperatures $T_N$. Furthermore, similar effective magnetic moments of $\mu_{\text{eff}} = (5.20 \pm 0.02) \mu_B$ for Li$_{0.5-\delta}$CoPO$_4$ and $\mu_{\text{eff}} = (5.08 \pm 0.02) \mu_B$ for Li$_{1-\gamma}$CoPO$_4$ were found. Both values exceed the spin-only value of high-spin Co$^{2+}$ and Co$^{3+}$ (3.9 $\mu_B$ and 4.8 $\mu_B$, respectively), demonstrating a non-negligible orbital contribution. Taking into account the finite angular momentum, effective magnetic moments of 5.2 $\mu_B$ and 5.5 $\mu_B$ for high-spin Co$^{2+}$ and Co$^{3+}$ in the O$_h$ symmetry ($^3t_{2g}$ and $^4t_{1g}$ ground state) are expected in the weak spin–orbit coupling limit. Assuming the presence of only Co$^{2+}$ in the Li$_{1-\gamma}$CoPO$_4$ compound, the observed values are slightly smaller than the expected ones. However, the larger effective magnetic moment $\mu_{\text{eff}}$ of Li$_{0.5-\delta}$CoPO$_4$ clearly supports the findings of a mixed valence state of Co in the Li-deficient compound as discussed in the previous sections.

The inset of Fig. 5 reveals a more distinct difference of the magnetic properties of Li$_{1-\gamma}$CoPO$_4$ and the Li-deficient Li$_{0.5-\delta}$CoPO$_4$ compounds. LiCoPO$_4$ exhibits a magnetic double-hysteresis loop at 2 K, demonstrating an antiferromagnetic ground state at 0 T (for the hysteresis curves at 11 K and 300 K see Fig. S8, ESI†). Furthermore, the double-hysteresis loop indicates a spin-flip transition at a critical field of around $\pm 3$ T, which is much lower than for Pnma-type LiCoPO$_4$. Again, this can be attributed to the different structural properties. In contrast, an almost linear dependence of the magnetization as a function of the applied field is observed for Li$_{0.5-\delta}$CoPO$_4$ below $T_N$. No hysteresis with a finite remanence caused by a weak ferromagnetic phase due to the mixed-valence state of Co ions were found. However, the difference of the magnetic susceptibility recorded under field-cooled (FC) and zero field-cooled (ZFC) conditions suggests the formation of magnetic domains below $T \approx 5$ K. Below this temperature, the finite amount of Co$^{3+}$ ions as well as the observed defects on the Co sites might cause competing magnetic interactions resulting in a complex antiferromagnetic state as, for instance, described by Jensen and co-workers.

**Thermal stability**

The thermal stability of Li$_{0.5-\delta}$CoPO$_4$ (Cmcm) was investigated using TGA/DSC (Fig. 6) and temperature-dependent in situ X-ray powder diffraction, both performed under air (Fig. 7). The thermal behavior of LiCoPO$_4$ (Cmcm) has been discussed in detail in ref. 21. In the TGA curve (Fig. 6a), an overall mass loss of $\sim 4.8$ wt% is observed between 30 °C and 900 °C, which proceeds in several steps. The mass loss of $\sim 1.3$ wt% up to 360 °C is probably correlated with the decomposition of residues of the TTEG solvent and the acetate precursors (cf. CHNS analysis, Table 2). The DSC curve shows two pronounced, broad endothermic peaks at 394 °C and 686 °C, respectively, with the first signal being accompanied by a weight loss step of $\sim 2.5$ wt% and the second one of $\sim 0.1$ wt%. The corresponding X-ray powder diffraction pattern (Fig. 6b) reveals that a mixture of 44.9(6) wt% olivine-type LiCoPO$_4$ (Pnma, ICSD no. 431999) and 55.1(6) wt% of the low-temperature modification of cobalt pyrophosphate, $\alpha$-Co$_2$P$_2$O$_7$ (P2$_1$/c, ICSD no. 280959) was formed. Note that data obtained from a similar experiment using an argon atmosphere are in good agreement (Fig. S9 and S10, Tables S12–S16, ESI†).

In order to understand the signals observed in the TGA/DSC study and to identify possible intermediates of the heating process, we performed a temperature-controlled in situ PXRD experiment between room temperature (30 °C) and 900 °C with a step size of 100 °C (Fig. 7). The Rietveld fits of the individual PXRD patterns at each temperature up to 700 °C can be found in Fig. S11 (ESI†). The refined phase fractions and crystallographic details (atomic coordinates, thermal displacements parameters, bond lengths), reflecting the structural changes, are presented in Tables S17–S23.† (Note that the patterns at $T \geq 800$ °C, which are shown in Fig. S12 (ESI†), were of insufficient quality for a refinement because of the occurrence of strong reflections from the corundum sample holder.) Up to 300 °C, no change of...
the endothermic DSC signal at 395 °C can be explained by the decomposition of Li$_{0.55}$CoPO$_4$ (Cmcm) to these phases (the simultaneous mass loss will be explained later in the text). Between 500 °C and 600 °C, the Cmcm-type Li$_{1-x}$CoPO$_4$ intermediate starts to convert to the thermodynamically more stable olivine Pnma structure, whereas the peaks of α-Co$_2$P$_2$O$_7$ remain unaltered. The fact that the low-temperature α-modification of Co$_2$P$_2$O$_7$ (P2$_1$/c) does not transform to the high-temperature β-Co$_2$P$_2$O$_7$ (A2/m) phase, which would be expected at ~480 °C (ref. 48) for the pure material, suggests that the transformation is either kinetically hindered or very slow. Hence, the DSC signal at 688 °C corresponds to the transformation of the Cmcm to the Pnma LiCoPO$_4$ phase. The lower transition temperature found in the in situ PXRD study compared to the DSC data might be related to slightly different atmospheres (air vs. synthetic air) and heating rates (10 °C min$^{-1}$ vs. 5 °C min$^{-1}$) being used. The phase transformation is not completed until 700 °C because traces of Li$_{1-x}$CoPO$_4$ (Cmcm) can be identified in the diffraction pattern at 600 °C. Compared to the thermal stability of the pure, lithiated LiCoPO$_4$ (Cmcm) material (transformation to single-phase LiCoPO$_4$ (Pnma) at 575 °C), the phase transition temperature is significantly increased. No further phase changes are observed in the PXRD patterns up to 700 °C, yet the diffraction peaks are shifted to lower angles, indicating bigger lattice dimensions due to thermal expansion. Unfortunately, it cannot be derived from the patterns at $T \geq 800$ °C (see Fig. S12, ESI†) whether the Pna2$_1$-type LiCoPO$_4$ structure reappears as a high-temperature phase as reported for all three, fully lithiated LiCoPO$_4$ polymorphs (Pna2$_1$, Pna2$_1$, and Cmcm). The pattern of the cooled sample (25 °C; Fig. S12, ESI†) is consistent with the ex situ PXRD experiment (Fig. 6b) and shows reflections of α-Co$_2$P$_2$O$_7$ and Pnma-type LiCoPO$_4$, indicating that both phase transitions are irreversible.

The results of the thorough investigation of the thermal stability of the Li-deficient compound Li$_{0.55}$CoPO$_4$ demonstrate that the phase exhibits a complex behavior upon heating which involves several phase transitions. Based on the combined approach using TGA, DSC (Fig. 6), and in situ PXRD studies (Fig. 7), a decomposition mechanism can be proposed according to Scheme 1. Note that since it is not possible to determine the composition of the decomposition products and intermediates (which are likely to be deficient in Li and Co as well), the mechanism is presented on basis of the nominal composition Li$_{0.55}$CoPO$_4$ with $\delta = 0$. In the first step (eqn (I)), LiCoPO$_4$ (Cmcm) and Co$_2$P$_2$O$_7$ (P2$_1$/c; both with Co oxidation state +2) are formed from four equivalents of the Co$^{2+}$/Co$^{3+}$ mixed-valent starting material Li$_{0.55}$CoPO$_4$ (Cmcm). This step is based on a redox reaction, in which the two Co$^{3+}$ equivalents from the four Li$_{0.55}$CoPO$_4$ (6 = 0) units are reduced by O$^{2-}$ ions (eqn (Ia)), which are released upon the pyrophosphate formation (i.e., coupling of isolated [PO$_4$] tetrahedra to [P$_2$O$_5$] units via shared corners). The O$^{2-}$ ions are in turn oxidized to form elemental oxygen (eqn (Ib)) that is released. The O$_2$ release from the phosphate groups corresponds to an approximate mass loss of ~2.5 wt% which in full agreement with the TGA mass loss step observed at 394 °C (cf. Fig. 6a). The estimated mass fractions of Li$_{1-x}$CoPO$_4$ (Cmcm, with $\gamma = 0$) and Co$_2$P$_2$O$_7$ after the
Co$_2$P$_2$O$_7$ crystallization was found to be not proceeding simultaneously, but at higher temperature than the Li$_{0.5}$CoPO$_4$ ($Cmcm$) decomposition, which was related to a possibly amorphous intermediate. In addition, the decomposition process was suggested to be promoted by carbon present in samples, which reacts with the released oxygen to form CO$_2$ gas. The crucial influence/destabilizing effect of carbon on the thermal stability was also confirmed for charged LiCoPO$_4$ electrodes containing CoPO$_4$. Based on this work, however, there is no indication that carbon affects the decomposition of the pristine Li$_{0.5}$CoPO$_4$ ($Cmcm$) material since the carbon content of our material is not significant (0.4(3) wt%, cf. Table 2). To clarify whether this is also the case for the pristine, carbon-free Li$_{0.5}$CoPO$_4$ ($Cmcm$) material, future studies are needed for charged LiCoPO$_4$ electrodes, our direct synthetic approach might provide a pathway to get a deeper understanding of their intrinsic thermal stabilities as well.

### Conclusions

In this study, a polyol synthesis pathway towards the first Li-deficient structural derivative of the $Cmcm$ polymorph of LiCoPO$_4$ with the nominal composition Li$_{0.5}$CoPO$_4$ and its material properties were presented. To the best of our knowledge, this is also the first time that a sub-stoichiometric Li$_{\text{1-x}}$CoPO$_4$ phase was synthesized using a soft-chemical bottom-up approach as opposed to common chemical and electrochemical Li extraction techniques starting from LiCoPO$_4$-type materials.

Neutron and X-ray powder diffraction experiments as well as elemental analysis suggested that Li$_{0.5}$CoPO$_4$ ($Cmcm$) is non-stoichiometric and deficient both in Li and Co, which generates vacancies on both cation sub-lattices in the crystal structure. The occurrence of vacancies was also observed in the course of a structure redetermination of the ‘fully lithiated’ $Cmcm$ phase, resulting in the revised formula Li$_{1-x}$CoPO$_4$. Co was found to be partly coordinated to oxygen atoms, and the Li-deficient structure bears both Co$^{2+}$ and Co$^{3+}$ ions to compensate for the Li deficit. Due to the reduced Li content and amount of electrochemically active Co$^{2+}$ ions, the material exhibited a poor electrochemical performance. The thermal stability of Li$_{0.5}$CoPO$_4$ has been studied thoroughly using thermogravimetry, differential scanning calorimetry, and temperature-dependent in situ X-ray powder diffraction experiments. Li$_{0.5}$CoPO$_4$ ($Cmcm$) is metastable and shows a complex, two-step decomposition mechanism upon heating. At 394°C, it decomposes to α-Co$_2$P$_2$O$_7$ ($P2_1/c$) and Li$_{1-x}$CoPO$_4$ ($Cmcm$) in an endothermic reaction upon which oxygen is released as a result of a redox reaction. The Li$_{1-x}$CoPO$_4$ ($Cmcm$) phase then irreversibly converts to the thermodynamically more stable LiCoPO$_4$ ($Pnma$) olivine structure at 686°C.

To conclude, the present work paves the way towards the direct and simple soft-chemical preparation and investigation of Li-deficient structures derived from lithium transition-metal phosphates. Our methodology provides fundamental insights into the material properties, and hence to study Li-deficient intermediates that are probably involved in the charge/discharge steps of LiCoPO$_4$-type cathodes. It further helps to understand the complex structure chemistry of this class of cathode materials for Li-ion batteries. In that matter, future studies should focus on compositional tuning (e.g. by...
modifying the amounts of the precursors in the synthesis) in order to identify other partially lithiated structural derivatives.

**Author contributions**

J. L. performed the material characterization using in situ and ex situ PXRD, SEM/EDS, IR spectroscopy, and electrochemical measurements, and analyzed the data (under supervision of T. N. and M. M. D.). C. A.-S. performed the synthesis. S. G. and D. N. performed and analyzed magnetic and XAS measurements, respectively. I. P. O. and C. A.-S. conducted neutron diffraction experiments. J. L. wrote the manuscript. All authors have given approval to the final version of the manuscript.

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**Abbreviations**

AAS | Atomic absorption spectroscopy  
AEY | Auger electron yield  
DFT | Density functional theory  
DSC | Differential scanning calorimetry  
EDS | Energy-dispersive X-ray spectroscopy  
FC | Field-cooled  
FTIR | Fourier-transform infrared  
FY | Fluorescence yield  
HS | High-spin  
ICSD | Inorganic Crystal Structure Database  
LS | Low-spin  
NPD | Neutron powder diffraction  
PXRD | Powder X-ray diffraction  
SEM | Scanning electron microscope  
SQUID | Superconducting quantum interference device  
TEY | Total electron yield  
TGA | Thermogravimetric analysis  
TTEG | Tetraethylene glycol  
XAS | X-ray absorption spectroscopy  
ZFC | Zero field-cooled

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