

Lawrence Berkeley National Laboratory

Energy Storage & Distributed Resources

Title

Co₁₁Li[(OH)₅O][(PO₃OH)(PO₄)₅], a Lithium-Stabilized, Mixed-Valent Cobalt(II,III) Hydroxide Phosphate Framework

Permalink

<https://escholarship.org/uc/item/56q0958s>

Journal

Inorganic Chemistry, 56(18)

ISSN

0020-1669

Authors

Ludwig, Jennifer
Geprägs, Stephan
Nordlund, Dennis
[et al.](#)

Publication Date

2017-09-18

DOI

10.1021/acs.inorgchem.7b01152

Peer reviewed

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

**Co₁₁Li[(OH)₅O][(PO₃OH)(PO₄)₅], a Lithium-Stabilized,
Mixed-Valent Cobalt (II,III) Hydroxide Phosphate
Framework**

Journal:	<i>Inorganic Chemistry</i>
Manuscript ID	Draft
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Ludwig, Jennifer; Technical University of Munich, Department of Chemistry Geprägs, Stephan; Bayerische Akademie der Wissenschaften, Walther- Meißner-Institut Nordlund, Dennis; Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory Doeff, Marca; Lawrence Berkeley National Laboratory, Energy Storage and Distributed Resources Division Nilges, Tom; Technical University of Munich, Department of Chemistry

SCHOLARONE™
Manuscripts



a Lithium-Stabilized, Mixed-Valent Cobalt (II,III) Hydroxide Phosphate Framework

Jennifer Ludwig^{a,*}, *Stephan Geprägs*^b, *Dennis Nordlund*^c, *Marca M. Doeff*^d, and *Tom Nilges*^{a,*}

^a Technical University of Munich, Department of Chemistry, Synthesis and Characterization of Innovative Materials, Lichtenbergstr. 4, 85747 Garching, Germany

^b Walther Meissner Institute, Bavarian Academy of Sciences and Humanities, Walther-Meissner-Str. 8, 85747 Garching, Germany

^c Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575 Sand Hill Rd, Menlo Park, CA, 94025, USA

^d Lawrence Berkeley National Laboratory, Energy Storage and Distributed Resources Division, 1 Cyclotron Rd, Berkeley, CA, 94720, USA

KEYWORDS. Cobalt lithium hydroxide phosphate, hydrothermal synthesis, metastable compounds, crystal structure, thermal stability

1
2
3 ABSTRACT. A new metastable phase, featuring a lithium-stabilized mixed-valence cobalt (II,III)
4 hydroxide phosphate framework, $\text{Co}_{11.0(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$, corresponding to the
5 simplified composition $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$, is prepared by hydrothermal synthesis. Because
6 the pH-dependent formation of other phases such as $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ and olivine-type
7 LiCoPO_4 competes in the process, a pH value of 5.0 is crucial for obtaining a single-phase material.
8 The crystals with dimensions of $15 \mu\text{m} \times 30 \mu\text{m}$ exhibit a unique elongated triangular pyramid
9 morphology with a lamellar fine structure. Powder X-ray diffraction experiments reveal that the
10 phase is isostructural with the natural phosphate minerals holtedahlite and satterlyite, and
11 crystallizes in the trigonal space group $P31m$ ($a = 11.2533(4) \text{ \AA}$, $c = 4.9940(2) \text{ \AA}$,
12 $V = 547.70(3) \text{ \AA}^3$, $Z = 1$). The three-dimensional network structure is characterized by partially
13 Li-substituted, octahedral $[\text{M}_2\text{O}_8(\text{OH})]$ ($M = \text{Co}, \text{Li}$) dimer units which form double chains that
14 run along the $[001]$ direction and are connected by $[\text{PO}_4]$ and $[\text{PO}_3(\text{OH})]$ tetrahedra. Because no
15 Li-free $P31m$ -type $\text{Co}_2(\text{OH})\text{PO}_4$ phase could be prepared, it can be assumed that the Li ions are
16 crucial for the stabilization of the framework. Co L -edge X-ray absorption spectroscopy
17 demonstrates that the cobalt ions adopt the oxidation states +2 and +3 and hence, provides further
18 evidence for the incorporation of Li in the charge-balanced framework. The presence of three
19 independent hydroxyl groups is further confirmed by infrared spectroscopy. Magnetization
20 measurements imply a paramagnetic to antiferromagnetic transition at $T = 25 \text{ K}$ and a spin-glass-
21 like behavior with a blocking temperature of $\sim 9 \text{ K}$. The metastable character of the phase is
22 demonstrated by thermogravimetric analysis and differential scanning calorimetry, which above
23 $558 \text{ }^\circ\text{C}$ reveal a two-step decomposition to CoO , $\text{Co}_3(\text{PO}_4)_2$, and olivine-type LiCoPO_4 with
24 release of water and oxygen.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

INTRODUCTION

Transition-metal phosphates offer great structural and chemical diversity, which allows for interesting physical properties and therefore opens up a great portfolio of possible applications, for example in adsorption,¹ semiconductive glasses,² nonlinear optics,³ catalysis,⁴⁻⁷ and batteries.⁸⁻¹¹ In particular iron phosphates have been the object of considerable study because of the relative abundance of iron in nature,^{8, 12} whereas cobalt phosphates have been less investigated. An interesting catalyst for oxygen evolution reactions (OER) is, for example, the Co–Pi system, which contains mixed-valent Co ions in a complex hydroxide–hydrogen phosphate–phosphate environment.⁵⁻⁷ Since many natural phosphates represent hydrothermal minerals, the hydrothermal synthesis technique, mimicking nature, is a powerful tool for preparing compounds isostructural with natural minerals as well as original structures¹³ and hence, to further explore the class of cobalt phosphates.

The most prominent compound of this class is probably olivine-type LiCoPO₄ (space group: *Pnma*), which belongs to the group of lithium transition-metal orthophosphates LiMPO₄ (*M* = Fe, Mn, Co, Ni).⁸ The three-dimensional network structure hosts zigzag chains of [CoO₆] octahedra that run along the [001] direction and are connected by [PO₄] tetrahedra, whereas the Li ions are located in channels running along the [010] and [001] directions.⁸ LiCoPO₄ has been studied extensively in recent years because of its potential use as a high-voltage cathode material for lithium-ion batteries and high theoretical gravimetric energy density of 802 Wh·kg⁻¹, which might bring a significant improvement to current Li-ion battery technology.^{9, 10, 14-16} In addition, also the magnetic properties have been investigated in a number of studies,^{17, 18} revealing a weak ferromagnetic moment in the antiferromagnetic state below the Néel temperature of $T_N = 21.9$ K.

1
2
3 Because of their interesting magnetic characteristics, the class of cobalt hydroxide phosphates
4 has also been receiving increasing attention. The most important representative is $\text{Co}_2(\text{OH})\text{PO}_4$,
5
6 for which two polymorphs with orthorhombic (space group: $Pnmm$) and tetragonal ($I4_1/amd$)
7
8 structures are known.^{19, 20} The orthorhombic $\text{Co}_2(\text{OH})\text{PO}_4$ polymorph, which adopts the adamite
9
10 structure type ($\text{Zn}_2(\text{OH})\text{AsO}_4$, space group: $Pnmm$),^{21, 22} was first reported by Harrison and co-
11
12 workers¹⁹ in 1995. The three-dimensional network structure is built from chains of edge-sharing
13
14 $[\text{CoO}_4(\text{OH})_2]$ octahedra, which run along $[001]$ and are cross-linked by dimers of edge-shared
15
16 $[\text{CoO}_4(\text{OH})]$ trigonal bipyramids and $[\text{PO}_4]$ tetrahedra. The compound was found to be the first
17
18 ordered cobalt phosphate that exhibits a three-dimensional antiferromagnetic long-range order
19
20 below $T = 70$ K and a spin-glass-like state with a blocking temperature of 13 K. This spin-glass-
21
22 like behavior was related to a magnetic frustration of the Co^{2+} ions in the $[\text{CoO}_5]$ dimers due to the
23
24 existence of antiferromagnetic interactions between the neighboring $[\text{CoO}_6]_\infty$ chains as well as a
25
26 ferromagnetic interaction between the chains and the dimers.²³ In a number of studies by de Pedro
27
28 and co-workers,²⁴⁻²⁶ it was further demonstrated that the magnetic properties of adamite-type
29
30 $Pnmm$ - $\text{Co}_2(\text{OH})\text{PO}_4$ can be modified by substituting Co by other magnetic transition-metal ions
31
32 such as Ni, Cu, and Mn. Furthermore, also the properties of solid solutions of phosphate and
33
34 arsenate, $\text{Co}_2(\text{OH})(\text{PO}_4)_{1-x}(\text{AsO}_4)_x$ ($x = 0-1$), have been explored.²⁷

35
36 The tetragonal $\text{Co}_2(\text{OH})\text{PO}_4$ polymorph (space group: $I4_1/amd$) was recently reported by Wang
37
38 *et al.*²⁰ The phase is isostructural with the minerals caminite $\text{Mg}_{1.33}[\text{SO}_4(\text{OH})_{0.66}(\text{H}_2\text{O})_{0.33}]$
39
40 ($\text{MgSO}_4 \cdot \frac{1}{3} \text{Mg}(\text{OH})_2 \cdot \frac{1}{3} \text{H}_2\text{O}$)²⁸ and lipscombite $\text{Fe}_{2-y}(\text{OH})\text{PO}_4$ ($0 \leq y \leq 2/3$).²⁹ The three-
41
42 dimensional framework features chains of face-sharing $[\text{CoO}_4(\text{OH})_2]$ octahedra, which run along
43
44 the $[100]$ and $[010]$ directions and are connected by tri-bridging OH groups and $[\text{PO}_4]$ tetrahedra.
45
46 Magnetization experiments revealed a ferromagnetic moment below 20 K, which is most likely
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 caused by a canted, antiferromagnetic spin structure. Furthermore, a two-step switching of the
4 magnetization as a function of the magnetic field was found at 2 K. To explain this behavior, a
5 spin-flip component perpendicular to the crystallographic [001] direction and a spin-flop
6 component oriented along [001] were postulated.²⁰
7
8
9

10
11
12 In this work, we report on the hydrothermal synthesis and characterization of a new trigonal,
13 *P31m*-type cobalt hydroxide phosphate, which is stabilized by Li substitution and exhibits the
14 crystal-chemical composition $\text{Co}_{11.0(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$, simplified to
15 $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ for better comparability with the sum formula $\text{Co}_2(\text{OH})\text{PO}_4$ of the
16 adamite- (*Pnnm*) and caminite-type (*I4₁/amd*) materials. The phase is isostructural with the natural
17 phosphate minerals satterlyite^{30, 31} $\text{Fe}_{9.24}\text{Mg}_{2.76}(\text{OH},\text{O})_6(\text{PO}_3\text{OH})(\text{PO}_4)_5$ (found at the Big Fish
18 River area, Yukon Territory, Canada; simplified formula: $\text{Fe}_{1.54}\text{Mg}_{0.46}(\text{OH})\text{PO}_4$), and
19 holtedahlite³² $\text{Mg}_{12}(\text{OH},\text{O})_6(\text{CO}_3)_{0.24}(\text{PO}_3\text{OH})_{0.76}(\text{PO}_4)_5$ (from Modum, Norway; simplified:
20 $\text{Mg}_2(\text{OH})(\text{CO}_3)_{0.04}(\text{PO}_4)_{0.96}$) as well as its synthetic analogue $\text{Mg}_{12}(\text{OH},\text{O})_6(\text{PO}_3\text{OH})(\text{PO}_4)_5$
21 (simplified: $\text{Mg}_2(\text{OH})\text{PO}_4$).³³ The title compound is accessible at an intermediate pH value of 5.0
22 in the lithium–cobalt–(hydrogen) phosphate system, whereas the high-voltage cathode material
23 LiCoPO_4 and the cobalt hydroxide hydrogen phosphate $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ are formed under
24 alkaline (pH = 8.0) and acidic ($3.0 \leq \text{pH} \leq 4.5$) conditions, respectively. We therefore started to
25 discuss the structure of the title compound $\text{Co}_{11.0(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ first, before
26 briefly investigating synthetic aspects and physical properties, including infrared and X-ray
27 absorption spectroscopy, magnetic and thermal properties, in more detail.
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

EXPERIMENTAL SECTION

Hydrothermal Synthesis. $\text{Co}_{0.11(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ (or simplified: $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$) crystals were prepared by hydrothermal synthesis using a Berghof digestecTM pressure digestion system equipped with 50 mL teflon-lined (TFM-PTFE) stainless steel pressure vessels (DAB-2), a heating block (DAH-412), and a programmable temperature control unit (BTC-3000; NiCrNi temperature probe). The starting materials $\text{LiOH} \cdot \text{H}_2\text{O}$ (Bernd Kraft, $\geq 99.0\%$), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$ (Alfa Aesar, 98%), and $(\text{NH}_4)_2\text{HPO}_4$ (Merck EMSURE, $\geq 99.0\%$) were used in a Li:Co:P molar ratio of 2:1:1. First, 1.50 mmol $\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 1.50 mmol $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 20 mL deionized water (high-purity water type I, Millipore, 18.2 M Ω ·cm) to form a pink solution with pH = 5.5. A solution of 3.00 mmol $\text{LiOH} \cdot \text{H}_2\text{O}$ in 10 mL water was then added dropwise under continuous stirring. The pH of the resulting purple suspension (pH = 10) was adjusted to 5.0 using hydrochloric acid (Merck EMSURE, Ph. Eur., 37 wt%) with the help of indicator test strips (Merck MColorpHastTM, pH range: 2.0–9.0, pH graduation: 0.5) in order to obtain a phase pure material. To investigate the influence of the pH value on the phase formation, the pH of the reaction mixture was varied in a range of 3.0–8.0, with an increment step of 0.5, by adjusting the amount of HCl added. The mixture was stirred vigorously, transferred to the teflon-lined pressure vessel, and sealed quickly. The temperature was ramped to 220 °C within 2 h and kept at that temperature for 20 h, followed by natural cooling after the reaction. The violet precipitate (*cf.* TOC graphic) was recovered from the suspension (pH = 5.0) by filtration, washed five times with 25 mL deionized water and 25 mL absolute ethanol (VWR AnalaR NORMAPUR, 99.95%), and then dried in air at 150 °C for 12 h.

Powder X-ray Diffraction (PXRD) and Rietveld Refinements. PXRD data were collected using a Stoe STADI P diffractometer (Mo $K_{\alpha 1}$ radiation, Ge(111) monochromator, $\lambda = 0.70930 \text{ \AA}$)

1
2
3 equipped with a Dectris MYTHEN DCS 1K silicon solid-state detector. The ground powders were
4 sealed in borosilicate glass capillaries with a diameter of 0.5 mm (Hilgenberg), and then measured
5 for 12 h in a 2θ range of 3–60° (PSD step: 0.015°; time/step: 30 s, three ranges). Silicon powder
6 ($a = 5.43088 \text{ \AA}$) was used as external standard for the calibration of the patterns. Rietveld fitting
7 was performed with the Jana2006 software³⁴ using the structure solution of the isostructural
8 mineral satterlyite (simplified formula: $\text{Fe}_{1.54}\text{Mg}_{0.46}(\text{OH})\text{PO}_4$; structure-chemical formula:
9 $\text{Fe}_{9.24}\text{Mg}_{2.76}(\text{OH},\text{O})_6(\text{PO}_3\text{OH})(\text{PO}_4)_5$, space group: $P31m$, ICSD no. 94842)³¹ as a starting model.
10 The background profile was fitted using a Chebyshev polynomial (35 coefficients), and peak
11 asymmetry was corrected by the axial divergence model³⁵ embedded in Jana2006. An absorption
12 correction³⁶ was applied using an estimated packing fraction of 0.6 for the capillary. The general
13 atomic positions and isotropic thermal displacement parameters of the Co, P, and O atoms were
14 refined without restraints, whereas all parameters of the H atoms were kept fixed. Furthermore, a
15 Li substitution on both Co sites was assumed, while keeping the sum of the Li and Co site
16 occupancy factors at 1. The positional atomic parameters were then standardized using the
17 Structure Tidy routine³⁷ implemented in the Platon software package.³⁸ Finally, the Berar's factor³⁹
18 was applied to all refined parameters to obtain more realistic standard uncertainties.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 **Elemental Analysis.** The Li content was analyzed by atomic absorption spectroscopy (AAS)
42 using a Varian AA280FS sequential device. The Co and P amounts were measured by photometry
43 on a Shimadzu UV-160 instrument. A Hekatech Euro EA CHNSO analyzer was used to determine
44 the C, H, N, and S contents.
45
46
47
48
49

50 **Soft X-ray Absorption Spectroscopy (XAS).** Soft X-ray absorption spectroscopy (XAS)
51 measurements were performed at beamline 8-2 of Stanford Synchrotron Radiation Laboratory
52 (SSRL) using a 1100 mm^{-1} spherical grating monochromator (TGM) operated with 30 \mu m slits,
53
54
55
56
57
58
59
60

1
2
3 providing $\sim 2.0 \cdot 10^{10}$ ph·s⁻¹ at 0.4 eV resolution in a 1 mm² beam spot as described in our previous
4
5 work.¹⁴ The powder sample was spread onto double-sided carbon tape and five scans of the Co
6
7 *L*_{2,3}-edge μ (E) spectra were acquired under ultrahigh vacuum (10⁻⁹ Torr) at ambient temperature
8
9 in the Auger electron yield (AEY; probing depth: ~ 2 nm), total electron yield (TEY; 2–5 nm), and
10
11 fluorescence yield (FY; 50–100 nm) modes, respectively.⁴⁰ AEY was collected from a double-pass
12
13 cylindrical mirror analyzer at a pass energy of 200 eV, TEY was observed through the drain current
14
15 without bias, and FY was collected from a silicon diode (IRD AXUV-100) mounted at a higher
16
17 glancing angle to reduce saturation effects. The spectra were normalized to the incoming flux and
18
19 the energy scale aligned to meet the common energy scale of reference⁴¹, followed by a linear
20
21 background subtraction. The fitting, which was used to quantify the formal oxidation state of the
22
23 Co ions, was limited to a small energy region across the *L*₃ edge (774–784 eV). In order to further
24
25 experimentally evaluate the crystal field strength and symmetry, the experimental peak positions
26
27 were extracted from the second derivatives.
28
29
30
31
32
33

34 **Magnetic Measurements.** DC magnetization measurements were performed using a Quantum
35
36 Design MPMS XL7 SQUID (superconducting quantum interference device) magnetometer in the
37
38 temperature range of $T = 2$ –300 K under a magnetic field of up to 7 T. The powder sample was
39
40 prepared using a calibrated gelatin capsule placed in a homogenous plastic straw. The temperature-
41
42 dependence of the magnetic moment was measured in an applied magnetic field of 1 T after
43
44 cooling the samples under a magnetic field of 7 T (field-cooled, FC) and 0 T (zero-field-cooled,
45
46 ZFC). Magnetic hysteresis measurements were performed at magnetic field strengths between
47
48 –7 T and 7 T at temperatures of 2 K, 10 K, 20 K, and 30 K, respectively.
49
50
51
52

53 **Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).** The
54
55 thermal stability was assessed by simultaneous TGA/DSC using a Mettler Toledo 1 STAR system.
56
57
58
59
60

1
2
3 An alumina crucible was filled with a specimen weight of approximately 5 mg and then heated up
4
5 to 900 °C under an argon stream (10 mL·min⁻¹) at a heating rate of 10 °C·min⁻¹. Note that only the
6
7 heating cycle could be monitored due to the simultaneous instrument setup.
8
9

10 11 12 13 14 RESULTS AND DISCUSSION

15 16 Powder X-ray Diffraction and Rietveld Refinement

17
18 Fig. 1 shows the Rietveld fit of the as-prepared title compound
19
20 $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ (simplified formula for better comparability with the
21
22 adamite- (*Pnnm*)¹⁹ and caminite-type (*I4₁/amd*)²⁰ $\text{Co}_2(\text{OH})\text{PO}_4$ phases: $\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$),
23
24 which was obtained from the hydrothermal process at pH = 5.0. According to scanning electron
25
26 microscopy (SEM) (see inset of Fig. 1), the violet powder (*cf.* TOC graphic) consists of uniform
27
28 crystals (~15 μm × 30 μm) with a unique elongated triangular pyramid morphology and a lamellar
29
30 fine structure (for further details on the SEM analysis, please refer to the Supporting Information,
31
32 section 2, and Fig. S2). The PXRD pattern (see Fig. 1 and Fig. S1) is in good agreement with the
33
34 simulated patterns of the minerals satterlyite $\text{Fe}_{9.24}\text{Mg}_{2.76}(\text{OH},\text{O})_6(\text{PO}_3\text{OH})(\text{PO}_4)_5$ (space group:
35
36 *P31m*, *Z* = 1; ICSD no. 94842,³¹ simplified: $\text{Fe}_{1.54}\text{Mg}_{0.46}(\text{OH})\text{PO}_4$) and holtedahlite
37
38 ($\text{Mg}_{12}(\text{OH},\text{O})_6(\text{PO}_3\text{OH})(\text{PO}_4)_5$ (*P31m*, *Z* = 1; ICSD no. 64769,³³ simplified: $\text{Mg}_2(\text{OH})\text{PO}_4$),
39
40 suggesting that the phases are isostructural. In fact, all reflections can be fitted to the trigonal
41
42 structure model of satterlyite³¹ with good reliability factors (*R_p* = 4.04%, *R_{wp}* = 5.93%, χ^2 = 1.91;
43
44 *cf.* Table 1; for atomic coordinates, thermal displacements parameters, and selected interatomic
45
46 distances see Tables S7a and S8a). The unit cell volume of 547.70(3) Å³ lies between the Fe
47
48 (*V* = 562.71(9) Å³)³¹ and Mg (*V* = 539.3(3) Å³)³³ counterparts (for a detailed comparison of the
49
50 crystallographic data please refer to Table S1), which is in agreement with the trend of ionic radii
51
52
53
54
55
56
57
58
59
60

(with coordination number CN = 6) of Fe^{2+} (high-spin (HS): 0.78 Å), Co^{2+} (HS: 0.745 Å), and Mg^{2+} (0.72 Å)⁴² as well as the observed shifts in the PXRD patterns (Fig. S1).

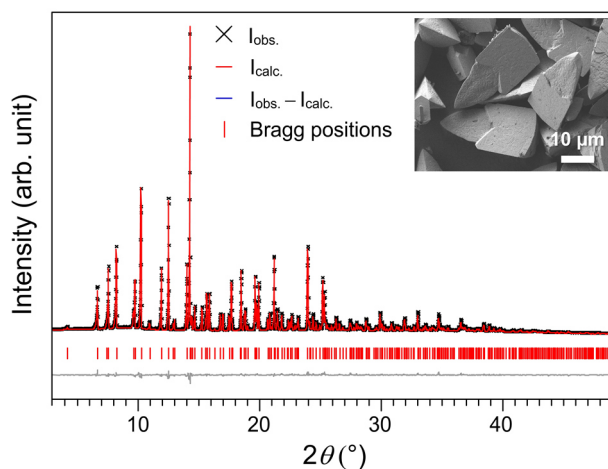


Figure 1. Rietveld fit of the powder X-ray diffraction data (Mo $K_{\alpha 1}$ radiation, 0.5 mm capillary, measurement time: 12 h) of $\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$ (crystal-chemical formula: $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$, space group: $P31m$, $Z = 1$) prepared by the hydrothermal process at pH = 5.0. Inset: Scanning electron microscopy image demonstrating that the sample consists of uniform, well-dispersed crystals with an elongated triangular pyramid morphology and dimensions of $\sim 15 \mu\text{m} \times 30 \mu\text{m}$.

Since the results of the elemental analysis suggested the presence of significant amounts of lithium in the material (see later in the discussion and Table 2), a partial substitution of the Co sites with Li was tentatively refined. The refinement resulted in statistically significant Li occupancies of 2.9(8)% on the Co1 site, and 12.2(8)% for the Co2 position. Mixed site occupation has also been reported for satterlyite, but with the divalent cation Mg^{2+} .³¹ Although the Li population on the Co1 site is rather low and hard to determine with X-rays, we concluded that Li–Co mixing appears on both sites because further studies showed that both sites show significant mixing for

Table 1. Crystallographic Parameters of $\text{Co}_{0.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$ as Refined from Powder X-ray Diffraction Data ($T = 298 \text{ K}$)^a

Simplified formula	$\text{Co}_{0.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$
Crystal-chemical formula	$\text{Co}_{0.85(1)}\text{Li}_{0.15(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$
M_r ($\text{g}\cdot\text{mol}^{-1}$)	1333.3
Space group (no.)	$P31m$ (157)
Z	1
a (Å)	11.2533(4)
c (Å)	4.9940(2)
V (Å ³)	547.70(3)
$F(000)$	645
ρ (calcd.) ($\text{g}\cdot\text{cm}^{-3}$)	4.038(1)
R_p	0.0404
R_{wp}	0.0593
R_{exp}	0.0326
R_F	0.0474
R_B	0.0647
χ^2	1.91
Data/restraints/parameters	3803/0/91

^a The standard deviations (in parentheses) were corrected using the Berar's factor.

the solid solutions with the general composition $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ at overall higher Li contents x (see later in the text and Fig. S7). Moreover, the free refinement of the Co occupancy factors (without Li substitution) indicated that both Co sites are not completely filled (occupancies: 97.3(7)% on Co1 and 88.1(7)% on Co2). These Co populations are comparable to the results of the Li/Co mixed model (occupancies: 97.1(8)% Co : 2.9(8)% Li on Co1/Li1 ($\equiv M1$) and 87.8(8)%

1
2
3 Co : 12.2(8)% Li on Co₂/Li₂ ($\equiv M_2$); see Table S7a). The crystal-chemical formula
4
5 Co_{11.1(1)}Li_{0.9(1)}[(OH)₅O][(PO₃OH)(PO₄)₅] ($Z = 1$; corresponding to a simplified bulk composition
6
7 of Co_{1.85(1)}Li_{0.15(1)}(OH)PO₄) is in good agreement with the composition derived from elemental
8
9 analysis (Co_{1.84(2)}Li_{0.16(3)}(OH)PO₄, *cf.* Table 2) and the molar Co:P:O ratio of
10
11 1.87(6):1.00(2):5.0(1) derived from EDS (energy-dispersive X-ray spectroscopy) analysis
12
13 (*cf.* Fig. S2). Note that this composition would not be charge-balanced assuming that the structure
14
15 contains only divalent Co²⁺ ions. However, X-ray absorption experiments discussed later reveal
16
17 that the deficit in positive electric charge due to the substitution by monovalent Li⁺ ions is
18
19 compensated by a corresponding amount of trivalent Co³⁺ in the framework.
20
21
22
23

24
25 The proton positions could not be refined from the X-ray data due to the low atomic scattering
26
27 factor of H, but the infrared (IR) spectrum (*cf.* Fig. S5) revealed the presence of three independent
28
29 hydroxyl groups, which is consistent with the literature.^{32, 43} The proton distribution in satterlyite
30
31 and holtedahlite has been a subject of thorough discussions in the literature.^{31, 33, 43} Whereas the
32
33 H1 and H2 positions, which are bonded to O ligands of [MO₆] octahedra (see structure discussion)
34
35 could be localized, the position of H3, which belongs to a hydrogen phosphate [PO₃(OH)] unit, is
36
37 strongly disordered in both structures and was not detectable in synthetic holtedahlite.³³ Although
38
39 there are seven possible proton positions in the structure (3 × H1, 3 × H2, and 1 × H1, *cf.*
40
41 Table S7a), the CHNS analysis of our compound (*cf.* Table 2) indicated that the asymmetric unit
42
43 contains only six protons. This is in agreement with the findings for the Mg and Fe counterparts,^{31,}
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Co_{11.1(1)}Li_{0.9(1)}[(OH)_{6-x}O_x][(PO₄)_{1-x}(PO₃OH)_x](PO₄)₅ (with $Z = 1$) because P3, which belongs to

1
2
3 the hydrogen phosphate group, has the multiplicity $\times 1$ (*cf.* Table S7a). Hence, the compound does
4
5 not represent a polymorph of $\text{Co}_2(\text{OH})\text{PO}_4$ in the strict sense, although the deviation from the ideal
6
7 composition is small. A theoretical end-member without a hydrogen phosphate unit (*i.e.*, $x = 0$)
8
9 would be $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}(\text{OH})_6(\text{PO}_4)(\text{PO}_4)_5$, which is equivalent to $6 \times [\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4]$.
10
11 However, this configuration seems to be unlikely since we could distinguish three hydroxyl bands
12
13 in the infrared spectrum, one of which is related with the $[\text{PO}_3(\text{OH})]$ group (for a detailed
14
15 discussion of the IR spectrum, please refer to the Supporting Information, section 3 and Fig. S5).
16
17
18
19
20
21

22 Crystal Structure

23
24
25 The structure of $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ features octahedral $[\text{MO}_6]$ ($M = \text{Co}$,
26
27 Li) and tetrahedral $[\text{PO}_4]$ building units that are connected to form a three-dimensional network.
28
29 The M positions are characterized by two crystallographically independent Co sites that are
30
31 partially substituted with Li. With 12.2(8)% Li, the $M2$ site is found to be richer in Li content than
32
33 $M1$, which is substituted by 2.9(8)% Li (*cf.* Table S7a). The corresponding $[(M1)\text{O}_6]$ and $[(M2)\text{O}_6]$
34
35 octahedra are distorted and show $M1\text{--O}$ distances in the range of 1.94(3)–2.25(3) Å ($d_{\text{av}} = 2.11$ Å),
36
37 and $M2\text{--O}$ distances of 2.10(2)–2.319(15) Å ($d_{\text{av}} = 2.19$ Å). The fact that the average $M\text{--O}$
38
39 distances in the $[(M2)\text{O}_6]$ units, which are more highly substituted with Li, are slightly larger than
40
41 in $[(M1)\text{O}_6]$ is consistent with the larger ionic radius of Li^+ compared to Co^{2+} (Li^+ : 0.76 Å; Co^{2+}
42
43 (HS): 0.745 Å).⁴² However, taking into account the finite amount of Co^{3+} in the structure (see XAS
44
45 discussion) and assuming that Li^+ and Co^{3+} are occupying the same M sites to form charge-
46
47 balanced $[\text{MO}_6]$ octahedra, a contraction of the $M2\text{--O}$ bond distance would be expected because
48
49 of the significantly smaller ionic radius of Co^{3+} (HS: 0.61 Å).⁴² Therefore, although it is not
50
51 possible to derive the $\text{Li}^+/\text{Co}^{2+}/\text{Co}^{3+}$ ordering in the structure without further experiments, it is
52
53
54
55
56
57
58
59
60

likely that due to energetic reasons and similar to other compounds,⁴⁴ the Co^{3+} ions preferably reside on the $M1$ sites whereas the Li^+ ions reside on the $M2$ sites, which would be consistent with the $M1\text{--O}$ and $M2\text{--O}$ distances.

The three P positions are represented by three unique, distorted $[\text{PO}_4]$ tetrahedra with average P–O distances of 1.52 Å (P1–O), 1.58 Å (P2–O), and 1.54 Å (P3–O). Each of these units is distorted, and one longer and three shorter bonds are observed (*cf.* Table S8a). The P3 tetrahedron is further characterized by a hydroxyl group (O9–H3), giving rise to $[\text{PO}_3(\text{OH})]$ hydrogen phosphate units, with the proton H3 being strongly disordered, as discussed earlier.

The $[(M1)\text{O}_6]$ and $[(M2)\text{O}_6]$ octahedra are condensed via shared faces ($M1$: O3, O4, O5; $M2$: O4, O5, O6; *cf.* Fig. 2a), forming $M1\text{--}M1$ respective $M2\text{--}M2$ pairs with $d(M1\text{--}M1) = 2.815(6)$ Å and $d(M2\text{--}M2) = 2.860(8)$ Å. Interestingly, the resulting dimer units $[(M1)_2\text{O}_8(\text{OH})]$ and $[(M2)_2\text{O}_8(\text{OH})]$ feature *cis*-configured μ_2 -bridging hydroxyl groups (O4–H1 and O5–H2), which has been confirmed by infrared spectroscopy (*cf.* Fig. S5). Note that although the calculation of O–H distances is not reliable using powder X-ray diffraction, the IR spectrum qualitatively confirms the presence of different force constants and hence, bond lengths.

The $[(M1)_2\text{O}_8(\text{OH})]$ and $[(M2)_2\text{O}_8(\text{OH})]$ dimers of face-sharing $[\text{MO}_6]$ octahedra are further linked by shared edges (O1–O4 and O2–O5) to form alternating double strands which run parallel to the $[001]$ direction and represent the dominant feature of the structure (Fig. 2b–d). As indicated in Fig. 2e, each double chain shares corners with six further double chains, reflecting the trigonal symmetry of the structure. The three independent $[\text{PO}_4]$ tetrahedra are located in the channels of the resulting three-dimensional framework that run along $[001]$. Whereas the $[(P1)\text{O}_4]$ and $[(P2)\text{O}_4]$ units are linked *via* all four corners, the $[(P3)\text{O}_3(\text{OH})]$ group shares only three apical O atoms with the network.

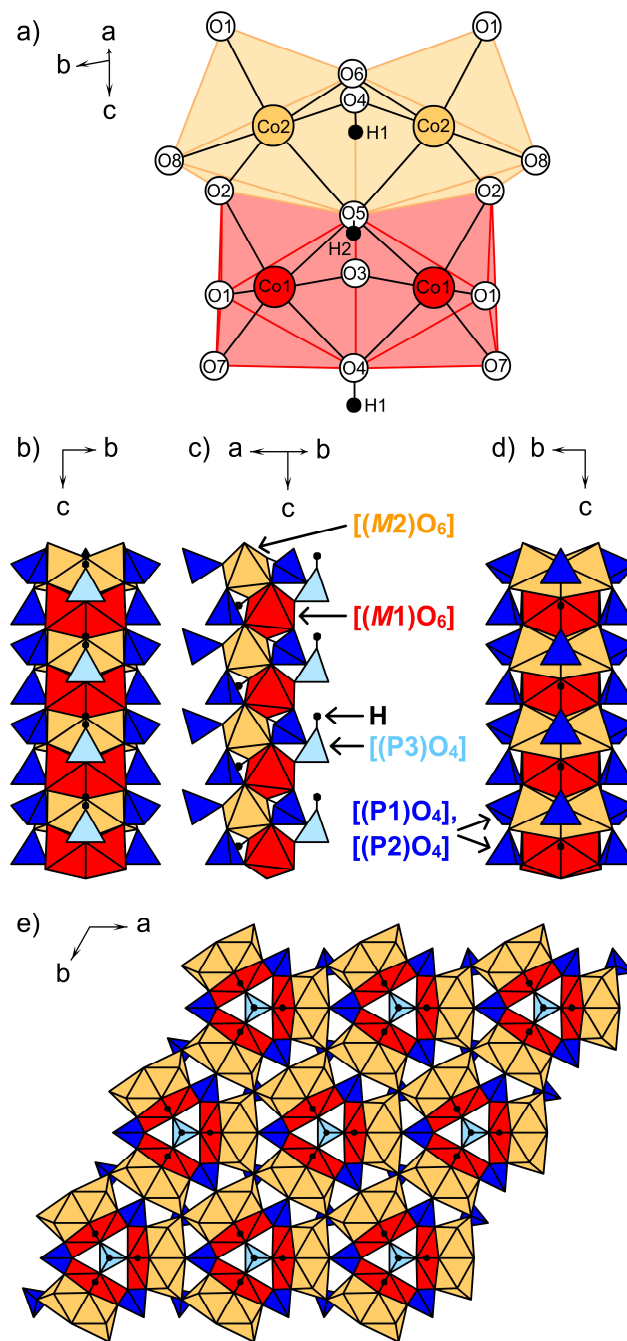


Figure 2. Polyhedral representation of the crystal structure of $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ (space group: $P31m$, $Z=1$; simplified formula: $\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$). (a) The structure features two independent M ($M = \text{Co}, \text{Li}$) sites, $M1$ (red; populations: 97.1(8)% Co, 2.9(8)% Li) and $M2$ (orange; 87.8(8)% Co, 12.2(8)% Li), which are coordinated by O atoms (white) in an octahedral geometry. The $[(M1)\text{O}_6]$ (red) and $[(M2)\text{O}_6]$

1
2
3 (orange) units form face-sharing $[(M1)_2O_8(OH)]$ and $[(M2)_2O_8(OH)]$ dimers with μ_2 -bridging OH
4 groups (H: black; occupancy: 83.3%). (b–d) Through edge-sharing of the dimers along [001],
5
6 alternating double chains are formed (viewed along different directions), which represent the
7
8 dominant structural motif. (e) The double chains are further connected by three different,
9
10 tetrahedral $[PO_4]$ units to form a three-dimensional network in which each double chain shares
11
12 corners with six other double chains. Whereas the $[(P1)O_4]$ and $[(P2)O_4]$ tetrahedra (dark blue)
13
14 share all apical O atoms with the network, the $[(P3)O_3(OH)]$ group (light blue) only contributes
15
16 three O atoms.
17
18
19
20
21
22
23
24

25 **Elemental Analysis**

26
27 Table 2 compares the results of the elemental analysis of the XRD-pure sample with the
28
29 theoretically expected values of a Li-free $Co_2(OH)PO_4$ material as well as the expected values
30
31 based on the refined composition $Co_{1.85(1)}Li_{0.15(1)}(OH)PO_4$ from the PXRD data. The CHNS
32
33 analysis indicates that the sample does not contain any detectable amounts of nitrogen or carbon,
34
35 which might be present due to residues or decomposition products of the $(NH_4)_2HPO_4$ and
36
37 $Co(CH_3COO)_2 \cdot 4 H_2O$ precursors. This demonstrates that the washing step is sufficient to remove
38
39 any side products formed in the synthesis. In contrast, 0.5(3) wt% H are found, which can be
40
41 correlated to the hydroxyl groups in the structure as demonstrated by IR spectroscopy (see later in
42
43 the discussion). Entrapped water as a possible source for hydrogen can be clearly ruled out because
44
45 no water absorption bands are observed in the IR spectrum (*cf.* Fig. S5).
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 2. Elemental Composition of (c) the As-Synthesized Material at pH = 5.0 in Comparison with the Theoretically Expected Values for (a) a Li-Free $\text{Co}_2(\text{OH})\text{PO}_4$ -Type Phase and (b) the Composition Derived from X-ray Diffraction^{a,b}

Element	a) Theoretical (Li-free phase)	b) Theoretical (expected from XRD) ^c	c) Measured
H (wt%)	0.4	0.5	0.5(3)
Co (wt%)	51.3	49.1(2)	49.0(5)
Li (wt%)	0	0.50(3)	0.5(1)
P (wt%)	13.5	13.9	14.0(3)
O(estd.) (wt%)	34.8	36.0	36(2) ^d
$n(\text{H}):n(\text{P})$	1:1	1:1	0.99(7):1.00(2)
$n(\text{Co}):n(\text{P})$	1:1	1.85(1):1	1.84(2):1.00(2)
$n(\text{Li}):n(\text{P})$	0	0.15(1):1	0.16(3):1.00(2)
$n(\text{O}):n(\text{P})$	5:1	5:1	5.0(3):1.00(2)
Empirical formula	$\text{Co}_2(\text{OH})\text{PO}_4$	$\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$	$\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})_{0.99(7)}\text{PO}_4$

^a The molar composition was determined from the experimental results (in wt%) of the CHNS, AAS, and photometric analyses, which were normalized to the P content (standard deviations are provided in parentheses). ^b The C, N, and S values were below the detection limit (= 0). ^c Note that standard deviations are only provided for the Co and Li contents since all other atomic sites were assumed to be fully occupied in the structure determination, and hence, do not exhibit standard deviations (see also Table S7a). ^d The O content was estimated from the H, Co, Li, and P contents (in wt%) based on the assumption that the sum of these elements accounts for 100 wt%.

In comparison to the ideal composition of a Li-free $\text{Co}_2(\text{OH})\text{PO}_4$ phase (Table 2a), which was suggested for the *Pnnm* and *I4₁/amd* polymorphs,^{23, 24} a considerable amount of Li (0.5(1) wt%; *i.e.* significant within three standard deviations) is found in the as-prepared *P31m*-type compound whereas the Co content shows a deficit of approximately 2.2 wt% (Table 2c). The corresponding Li:Co:P molar ratio of 0.16(3):1.84(2):1.00(2) suggests that Co (starting from two equivalents Co

1
2
3 in the idealized, Li-free composition $\text{Co}_2(\text{OH})\text{PO}_4$ is partially substituted by Li, which agrees with
4
5 the X-ray diffraction experiments (Table 2b). Taking into account the H and O contents, the
6
7 empirical formula of the material on the basis of the elemental analysis is $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$
8
9 (from this point on, this formula is used for the pure material synthesized at $\text{pH} = 5.0$ for
10
11 simplicity).
12
13
14
15
16
17

18 **Synthesis Parameters**

19
20 In order to gain further insights into the phase formation of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ (general
21
22 formula with varying Li contents x : $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$), the influence of reaction conditions on the
23
24 hydrothermal process based on the precursor system $\text{LiOH} \cdot \text{H}_2\text{O} - \text{Co}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O} -$
25
26 $(\text{NH}_4)_2\text{HPO}_4$ was systematically investigated. While the temperature and reaction time
27
28 demonstrated only minor influences, with the formation of the metastable $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ being
29
30 preferred at low temperatures and shorter reaction times due to kinetic reaction control (not
31
32 shown), the synthesis proved to be extremely sensitive towards the pH value of the reaction
33
34 mixture. Upon variation of the pH value in a range of 3.0–8.0 (increment step: 0.5), a variety of
35
36 Co-phosphates other than $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$, namely the phases $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ (space group:
37
38 $P2_1/c$, ICSD no. 67489)⁴⁵ and olivine-type LiCoPO_4 ($Pnma$, ICSD no. 431999),¹⁶ were obtained.
39
40 For pH values ≤ 2.5 , no precipitate was formed from the reaction, suggesting that all components
41
42 remained dissolved under strongly acidic conditions. The refined phase fractions *versus* the pH
43
44 value of the reaction mixture are shown in Fig. 3 (for the individual Rietveld fits and details on the
45
46 refinements please refer to Fig. S6 and Tables S4–S10 in the Supporting Information). Under
47
48 acidic conditions at $3.0 \leq \text{pH} \leq 4.5$, the formation of phase pure $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ is favored,
49
50 while $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ and LiCoPO_4 compete as reaction products at $5.5 \leq \text{pH} \leq 7.5$. The pH at
51
52
53
54
55
56
57
58
59
60

which pure $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ (with $x = 0.15(1)$) is formed is restricted to a very narrow region around pH 5.0. At pH = 5.5, the synthesis already yields 6.8(7) wt% LiCoPO_4 as a side product. The LiCoPO_4 fraction rises strongly until a single-phase olivine material is obtained under alkaline conditions (pH = 8.0). At pH > 8.0, a mixture of LiCoPO_4 and $\text{Co}_{11}(\text{OH})_6(\text{HPO}_3)_8$ (space group: $P6_3mc$, ICSD no. 72431)⁴⁶ was obtained (not shown).

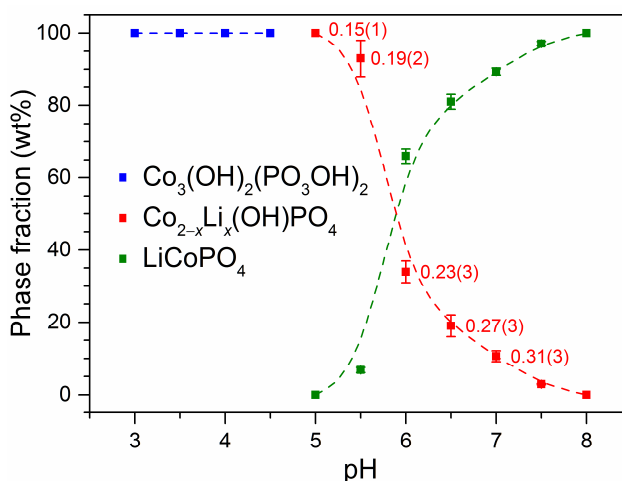
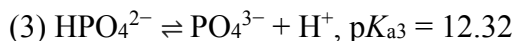
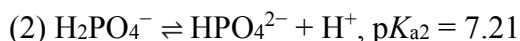
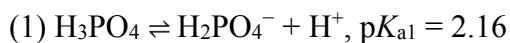


Figure 3. Phase fractions (in wt%; obtained from multi-component Rietveld refinements) versus pH value of the reaction mixture demonstrating that the formation of the phases $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ (space group: $P2_1/c$), $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ ($P31m$; the refined Li contents x are displayed in red along the data points for pH = 5.0–7.0 with standard deviations in parentheses), and LiCoPO_4 ($Pnma$) from the hydrothermal process is extremely pH-sensitive. It is evident that a pure $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ -type material is only realized at pH = 5.0. Non-visible error bars are smaller than the data points. Data points not shown correspond to a phase fraction of 0 wt%, meaning that no reflections of the respective phases were detected in the PXRD pattern.

The observed variation in reaction products strongly reflects the pH sensitivity of the hydrothermal process. One interesting aspect is that the phases $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$,

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

$\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$, and LiCoPO_4 involve phosphate groups with different degrees of protonation ($\text{HPO}_4^{2-} \rightarrow \text{HPO}_4^{2-}/\text{PO}_4^{3-}$ (*cf.* crystal structure) $\rightarrow \text{PO}_4^{3-}$). This can be related to the dissociation equilibria of phosphoric acid:⁴⁷



According to the $\text{p}K_{\text{a}}$ values, the predominant orthophosphate species in the pH range used for the hydrothermal synthesis (3.0–8.0) would be H_2PO_4^- (dihydrogen phosphate) and HPO_4^{2-} (hydrogen phosphate). However, under hydrothermal synthesis conditions, which involve high temperature and pressure and the presence of various reactants, the equilibria seem to be shifted towards HPO_4^{2-} and PO_4^{3-} . In this context, it is also worth noting that the phase fractions of $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ and LiCoPO_4 *versus* pH in Fig. 3 follow a trend that resembles the phosphate equilibrium curves. This is consistent with the fact that similar trends with respect to the phase formation were observed when alternative phosphate sources (such as *e.g.* H_3PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$) were used as starting materials (not shown). Furthermore, the cobalt and hydroxide contents per formula unit decrease with increasing pH value (Co^{2+} : $3 \rightarrow (2-x) \rightarrow 1$, OH^- : $2 \rightarrow 1 \rightarrow 0$), while the Li contents increase ($0 \rightarrow x \rightarrow 1$). This agrees with a report by Huang and co-workers,⁴⁸ who suggested that the formation of phases such as $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ and LiCoPO_4 is the result of a dissolution–recrystallization process involving $\text{Co}(\text{OH})_2$ as intermediate. The formation of Li-deficient phases in acidic media was related to the corrosion of the crystals and the solubility of LiOH under these conditions.

In agreement with this finding, the structure refinements reveal that the metal content and distribution in the individual phases is also affected by the pH value. In the case of

1
2
3 $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$, the Li content x (and hence, the Co^{3+} content) almost linearly increases in a
4 range of $0.15(1) \leq x \leq 0.31(3)$ with increasing pH value (Fig. 3 and Fig. S7a). There appears to be
5 a preference for Li substitution on the $M2$ site for all compositions $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$, although the
6 Li occupancies on the $M1$ site increase more rapidly with higher pH (see Table S7, Fig. S7a). The
7 cell volumes of $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ linearly decrease with increasing Li content x (Fig. S7b).
8 According to the ionic radii (CN = 6) of Li^+ (0.76 Å) and Co^{3+} (HS: 0.61 Å), *versus* Co^{2+} (HS:
9 0.745 Å),⁴² this decrease is mainly related to the concomitant increase of the Co^{3+} content, and
10 hence, is in good agreement with what is expected for solid solutions according to Vegard's law.⁴⁹
11 Despite the fact that the refinement of Li contents is not very reliable by means of X-ray methods
12 (*cf.* low atomic scattering factor of Li), this suggests that the phase displays a certain phase width.
13 Therefore, future experiments should focus onto compositional tuning of $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ in
14 order to identify the phase width and probably modify the material properties (*e.g.* by varying the
15 stoichiometry of the precursors). It has to be pointed out that within the scope of our investigations,
16 all attempts to prepare a Li-free $P31m$ - $\text{Co}_2(\text{OH})\text{PO}_4$ phase by using only $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$
17 and $(\text{NH}_4)_2\text{HPO}_4$ as precursors proved unsuccessful, resulting in single-phase $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$
18 as the product (not shown). This suggests that the $P31m$ -framework is probably stabilized by
19 partial Li substitution (up to ~16 at%) as opposed to the lithium-free $Pnmm$ and $I4_1/amd$
20 $\text{Co}_2(\text{OH})\text{PO}_4$ polymorphs. This would be in line with a report by Kolitsch *et al.*,³¹ who suggested
21 that a certain Mg content is necessary to stabilize the Fe homologue satterlyite. Whether a potential
22 $P31m$ -type $\text{Co}_2(\text{OH})\text{PO}_4$ is experimentally accessible, should be further investigated by optimizing
23 the synthesis parameters. On the other hand, the maximum Li content we found was $x = 0.31(3)$,
24 which suggests that there is also an upper substitution limit above which the olivine structure
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 LiCoPO₄ (*Pnma*) is apparently more stable. This might be explained the presence of more Co³⁺ in
4
5 the structure, which could intrinsically destabilize the metastable framework.
6
7

8 For LiCoPO₄, it was revealed that the phase is more prone to anti-site defects when prepared
9
10 with increasing pH values, with the Co amount on the Li positions increasing (*cf.* Table S9). Since
11
12 olivine-type LiCoPO₄ (*Pnma*) is a potential high-voltage cathode material for lithium-ion
13
14 batteries,^{8-10, 14-16} the investigation of the precursor system also provides valuable insights into this
15
16 class of materials. The occurrence of anti-site defects results in a blocking of the Li-diffusion
17
18 pathways, which reduces the electrochemical performance,⁵⁰ and hence suggests that the precursor
19
20 system and the alkaline medium are not suitable for the production for high-performance cathode
21
22 materials. The fact that LiCoPO₄ and Co_{2-x}Li_x(OH)PO₄ coexist over a wide pH range
23
24 (5.5 ≤ pH ≤ 7.5) is furthermore highly relevant for the production of the material. In fact, we
25
26 obtained Co_{2-x}Li_x(OH)PO₄ as a side phase with LiCoPO₄ using different solvothermal synthesis
27
28 conditions especially when the pH value was not optimized. This is also in line with a report⁵¹ on
29
30 another polymorph of LiCoPO₄ (space group: *Pna21*), for which the orthorhombic *Pnmm*-type
31
32 Co₂(OH)PO₄ polymorph was observed as a competing phase under non-ideal conditions.
33
34 Interestingly, reflections originating from *P31m*-type Co_{2-x}Li_x(OH)PO₄ were also evident in
35
36 PXRD patterns reported by other groups.⁵² However, the peaks were correlated with other phases
37
38 such as LiP₅, Li_{10.62}CoO₂, and CoO. For that matter, the investigations on Co_{2-x}Li_x(OH)PO₄ are
39
40 highly significant for the wet-chemical synthesis of Co-containing cathode materials. Whether the
41
42 homologue phases *M*_{2-x}Li_x(OH)PO₄ (*M* = Fe, Mn, Ni) exist and possibly also compete in the
43
44 synthesis of the olivine-type cathode materials LiMPO₄ (*M* = Fe, Mn, Ni) is an interesting topic
45
46 and should be investigated in consecutive studies.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

X-ray Absorption Spectroscopy

In order to investigate the oxidation state of the Co ions in the structure, soft X-ray absorption spectroscopy on the $L_{2,3}$ -edge was carried out, which is a powerful probe of the local electronic structure with sensitivity to symmetry, spin, valence, and covalency.^{53, 54} Fig. 4 shows the normalized Co L_3 -edge spectra of $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ compared to reference spectra of octahedrally coordinated (O_h , CN = 6) high-spin (HS) Co^{2+} (from CoO)⁴¹ and HS Co^{3+} (from $\text{Sr}_2\text{CoO}_3\text{Cl}$)⁵⁵. The $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ spectra are shown for both the TEY mode (Fig. 4b), probing about 2–5 nm deep, and the AEY mode (Fig. 4a), probing at the very top of the surface (~2 nm). Unfortunately, the more bulk-sensitive FY spectrum (~50–100 nm) was not of sufficient quality to be analyzed or discussed further and is therefore not shown.

It is clearly observed that the AEY (Fig. 4a) and TEY (Fig. 4b) spectra of $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ both show strong commonalities with the reference spectrum of O_h HS Co^{2+} (Fig. 4c) in shape and energy positions of the main features (in particular, the lowest energy peak or shoulder at 776.4 eV is characteristic of octahedrally coordinated Co^{2+}).⁴¹ It can thus be discerned that high-spin divalent Co ions in an octahedral crystal field dominate the spectrum, which is in agreement with the crystal structure that features octahedral $[\text{MO}_6]$ ($M = \text{Co}, \text{Li}$) units and the pink color of the powder (*cf.* TOC graphic). The minima of the second derivatives (*cf.* Fig. S8), which correspond to the experimental peak positions, reveal a small but significant shift in the peak positions of $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ (*i.e.* peak splitting) compared to the HS Co^{2+} reference which indicates an increased crystal field strength.⁴¹ Moreover, the increase of spectral weight for both the AEY and TEY modes at higher energies, which is associated with Co^{3+} (*cf.* Fig. 4d) indicate the presence of Co^{3+} . This is in line with charge-balance arguments, which suggest that the $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ framework bears mixed-valent (+2/+3) Co ions due to the

substitution of the Co sites by Li^+ ions. Provided that the lack of positive charge caused by the Li^+ substitution (0.16 eq per formula unit) is compensated by the same amount of Co^{3+} ions (0.16 eq), the expected Co^{3+} content would be $\sim 8.7\%$ ($0.16/1.84$; based on a total of 1.84 eq Co).

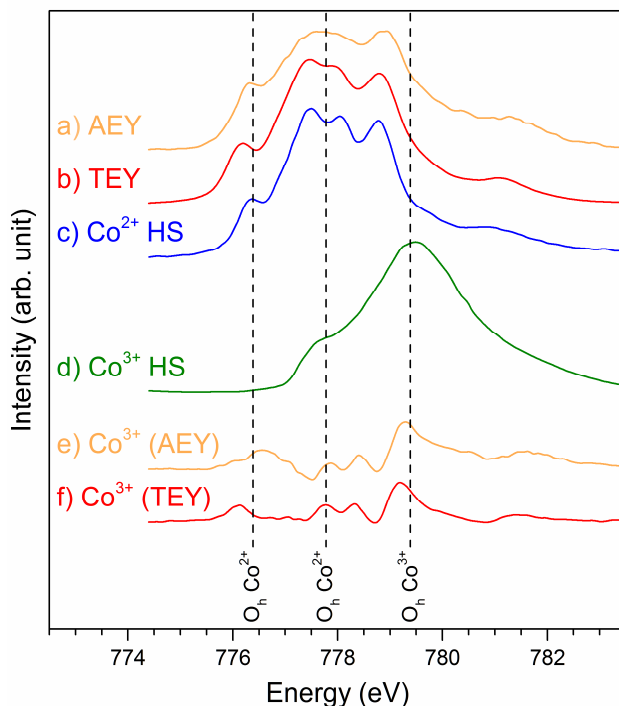


Figure 4. Normalized Co L_3 -edge XAS spectra of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ (prepared by hydrothermal synthesis at $\text{pH} = 5.0$) in the (a) AEY (orange) and (b) TEY (red) modes compared to reference spectra for octahedrally (O_h) coordinated (c) high-spin (HS) Co^{2+} (blue; CoO , adapted from ref. ⁴¹), and (d) high-spin (HS) Co^{3+} (green; $\text{Sr}_2\text{CoO}_3\text{Cl}$, adapted from ref. ⁵⁵). (e) and (f) show the difference spectra resulting from the subtraction of 15% and 6% Co^{2+} from the AEY and TEY spectra of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$, respectively, which represents the Co^{3+} contributions. The increased Co^{3+} contribution at the top surface (AEY, *cf.* a,e) compared to the bulk (TEY; *cf.* b,f) of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ is evident. All datasets have been aligned to match the common energy scale of reference ⁴¹. The vertical dashed lines indicate the energies corresponding to O_h Co^{2+} (characteristic shoulder: 776.4 eV; doublet: 777.7 eV) as well O_h Co^{3+} (779.4 eV).

1
2
3 In order to extract the formal oxidation state, the AEY and TEY spectra were fitted with both
4 high-spin Co^{2+} and Co^{3+} octahedral standards. The fitting of the TEY spectrum (*cf.* Fig. S9b)
5 reveals an average Co^{3+} contribution of around $(6.2 \pm 2.0)\%$, which is close to the expected Co^{3+}
6 content ($\sim 8.7\%$), whereas a higher Co^{3+} content of about $(14.6 \pm 5.0)\%$ was found for the most
7 surface-sensitive AEY mode (*cf.* Fig. S9a). It can therefore be concluded that the top surface
8 exhibits a higher Co^{3+} concentration than the bulk, which is also apparent from Fig. 4e,f,
9 representing the individual Co^{3+} contributions that were obtained from subtraction of the fitted
10 Co^{2+} contributions from the AEY and TEY spectra, respectively. This gradient in the Co^{3+}
11 concentration might be explained by the formation mechanism. In order to obtain an electronically
12 balanced, Li-bearing framework, part of the Co^{2+} ions are probably oxidized to Co^{3+} *in situ*,
13 compensating for the lack of positive charge due to the Li^+ substitution. It is likely that the
14 oxidation preferably occurs on the particle surface since Co^{2+} is generally prone to oxidation in
15 aqueous media. Therefore, it will be worth examining whether the Co oxidation (and Li
16 substitution) can be hindered by using reducing agents such as glucose, ascorbic acid or
17 hydrazine^{14, 50} in the reaction mixture in order to produce a Li-free, Co^{2+} -only *P31m*- $\text{Co}_2(\text{OH})\text{PO}_4$
18 framework.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

43 **Magnetic Properties**

44
45 The magnetic properties of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ are presented in Fig. 5. In the high
46 temperature regime ($T > 100$ K), the magnetic susceptibility measured using a magnetic field of
47 1 T in field-cooled (FC) and zero-field-cooled (ZFC) conditions follow a Curie–Weiss law with a
48 Weiss temperature of (-68 ± 2) K and an effective magnetic moment of $(7.08 \pm 0.05) \mu_{\text{B}}$ (see
49 Fig. S10). The negative Weiss temperature indicates that the dominant interaction between
50
51
52
53
54
55
56
57
58
59
60

1
2
3 neighboring magnetic ions is antiferromagnetic. This is in agreement with reports on the Li-free
4
5 *Pnnm*- and *I4₁/amd*-type $\text{Co}_2(\text{OH})\text{PO}_4$ polymorphs.^{20, 23} The low-temperature behavior of the
6
7 magnetic susceptibility, however, is different from that of the reported $\text{Co}_2(\text{OH})\text{PO}_4$ phases. The
8
9 first maximum of the magnetic susceptibility at around $T = 25$ K together with an almost linear
10
11 magnetic field dependence of the magnetization at 10 K suggest the onset of a long-range
12
13 antiferromagnetic order of $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ below 25 K. This temperature is close to the
14
15 transition temperature of 20 K found in the tetragonal (*I4₁/amd*) modification of $\text{Co}_2(\text{OH})\text{PO}_4$,²⁰
16
17 while it is much lower than the transition temperature of 71 K of the orthorhombic (*Pnnm*)
18
19 $\text{Co}_2(\text{OH})\text{PO}_4$ polymorph.²³ Furthermore, a second maximum of the ZFC magnetic susceptibility
20
21 was found at around 9 K. Below this temperature, $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ exhibits a magnetic
22
23 hysteresis with a finite remanent magnetization (see inset of Fig. 5 and Fig. S11), demonstrating
24
25 the existence of a ferromagnetic component. However, no saturation of the magnetization is
26
27 observed up to 7 T. This behavior is similar to that of *Pnnm*- $\text{Co}_2(\text{OH})\text{PO}_4$ below 15 K,²³ indicating
28
29 a spin-glass-like behavior with a blocking temperature of around 9 K. However, to further
30
31 investigate this spin-glass-like behavior, AC-susceptibility measurements at different frequencies
32
33 would be required. In total, the finite Li^+ and Co^{3+} concentrations in the $\text{Co}_2(\text{OH})\text{PO}_4$ framework
34
35 results in a reduction of the paramagnetic to antiferromagnetic transition as well as the blocking
36
37 temperature of the spin-glass-like behavior. In order to unveil the structure-related magnetic details
38
39 unambiguously, neutron diffraction measurements will be required.
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

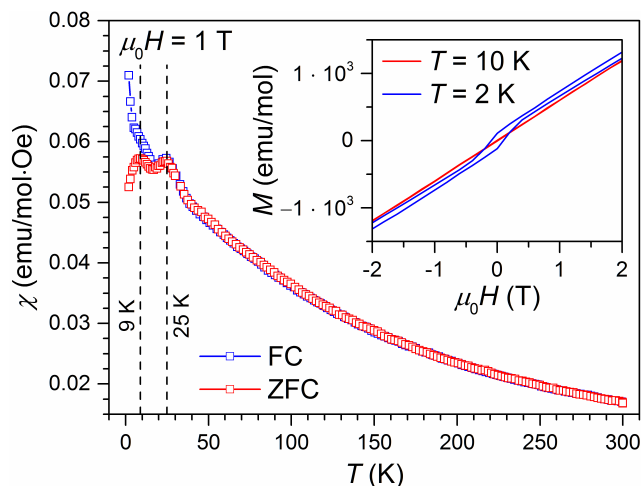


Figure 5. Magnetic susceptibility of $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ (prepared by hydrothermal synthesis at $\text{pH} = 5.0$) as a function of temperature measured at a magnetic field of 1 T under field-cooled (FC) and zero-field-cooled (ZFC) conditions. The vertical dashed lines indicate the temperature of the paramagnetic to antiferromagnetic transition (25 K) as well as the blocking temperature of the spin-glass-like behavior (9 K) at low temperature. Inset: Magnetic hysteresis curves measured at temperatures of $T = 10$ K and 2 K, respectively.

Thermal Stability

The thermal stability of $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ was investigated by TGA/DSC measurements, which demonstrate a metastable behavior of the material (Fig. 6a). Two signals are observed in the DSC curve, a small exothermic peak at 558 °C, and an endothermic peak at 663 °C. According to the TGA data, both transitions are accompanied by a weight loss that accounts for 4.6 wt% in total. The initial mass loss of about ~0.6 wt% starts around 440 °C, and is then followed by a distinct step of ~4.0 wt%. The fact that the weight loss onset occurs at rather high temperature implies that no residues of water or the cobalt acetate precursor are present (in agreement with the CHNS analysis, *cf.* Table 2), hence confirming the purity of the material.

1
2
3 According to the X-ray powder diffractogram of the dark violet post-TGA/DSC powder (Fig. 6b,
4 for details on the Rietveld refinement refer to Tables S11–S17), a mixture containing
5 72.3(10) wt% CoO (space group: $Fm\bar{3}m$; ICSD no. 9865),⁵⁶ 15.1(5) wt% $\text{Co}_3(\text{PO}_4)_2$ ($P2_1/c$, ICSD
6 no. 4268),⁵⁷ and 12.6(10) wt% olivine-type LiCoPO_4 ($Pnma$, ICSD no. 431999)¹⁶ was formed
7 upon heating. The formation of CoO and $\text{Co}_3(\text{PO}_4)_2$ upon decomposition is consistent with a
8 report¹⁹ on the $Pnmm$ polymorph of $\text{Co}_2(\text{OH})\text{PO}_4$, for which the same phases were observed (note
9 that for the $I4_1/amd$ polymorph, no decomposition products were reported²⁰). The occurrence of
10 the additional Li-containing phase LiCoPO_4 provides further evidence for the partial Li-
11 substitution of the $P31m$ -type $\text{Co}_2(\text{OH})\text{PO}_4$ framework.
12
13
14
15
16
17
18
19
20
21
22
23

24 Based on the TGA/DSC, *ex situ* PXRD as well as the XAS experiments, which demonstrated
25 the presence of Co^{3+} in the structure, the decomposition process of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ may
26 be described according to Fig. 6c. Whereas the second mass loss step of 4.1 wt%, which is
27 correlated with the endothermic signal around 663 °C, can most likely be attributed to the loss of
28 water from the hydroxyl groups of the framework (*cf.* $[\text{PO}_3(\text{OH})]$ and $[\text{M}_2\text{O}_8(\text{OH})]$ units), the small
29 initial weight loss of 0.6 wt% accompanying the exothermic peak around 558 °C may be the result
30 of oxygen release. This step is driven by a redox reaction, in which the O^{2-} ions are oxidized to
31 elemental O_2 (Eq. II) by the definite amount of Co^{3+} ions, which are in turn reduced to Co^{2+} (Eq. I).
32 The sum of the expected weight losses from H_2O and O_2 is consistent with the experimental TGA
33 mass loss of 4.6 wt% (*cf.* Fig. 6a). In total, the exothermic oxidation takes place first followed by
34 the endothermic dehydration step. Furthermore, the estimated mass fractions of the crystalline
35 decomposition products $\text{Co}_3(\text{PO}_4)_2$, CoO, and LiCoPO_4 in the solid residue after $\text{H}_2\text{O}/\text{O}_2$ release
36 are equivalent to the refined values obtained from our multi-component Rietveld analysis (Fig. 6b)
37 within one standard deviation, which further supports the suggested mechanism.
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

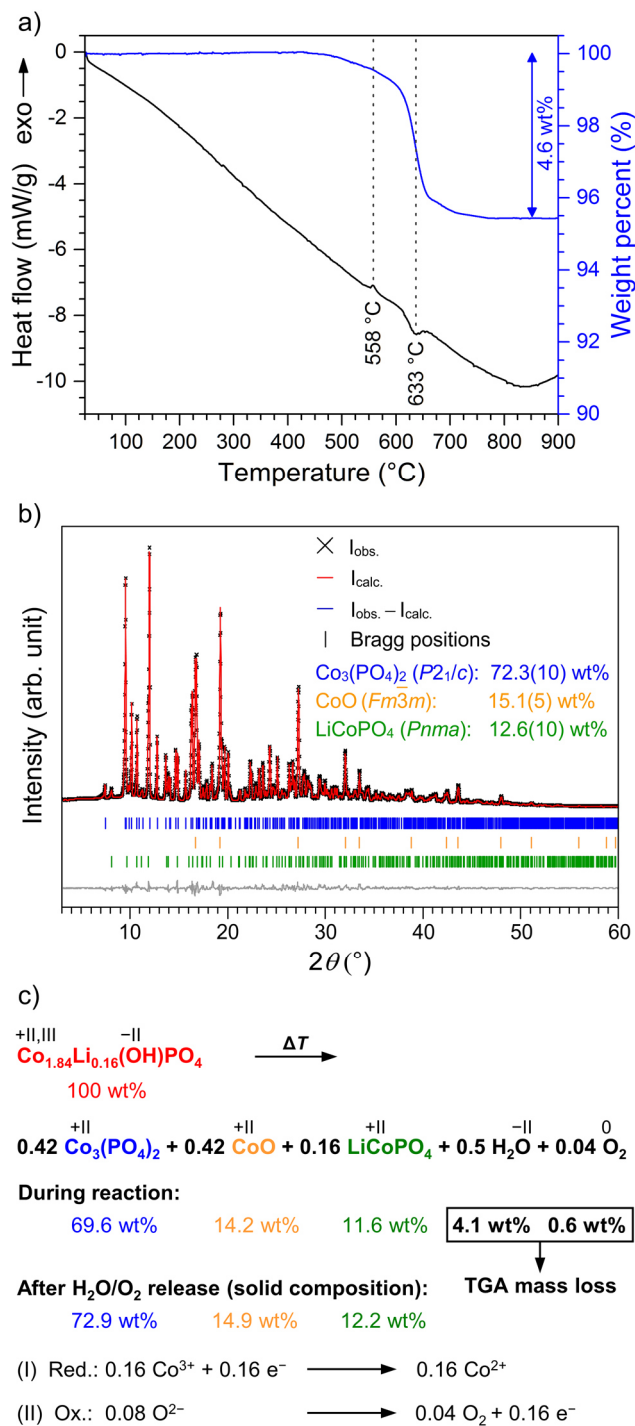


Figure 6. (a) DSC (black) and TGA (blue) curves of Co_{1.84(2)}Li_{0.16(3)}(OH)PO₄ measured under Ar in a temperature range of 30–900 °C (heating rate: 10 °C·min⁻¹). Two DSC signals are observed at 558 °C (exothermic) and 633 °C (endothermic), which are accompanied by a total weight loss

1
2
3 of 4.6 wt%. (b) Rietveld fit of the powder X-ray diffraction data (Mo $K_{\alpha 1}$ radiation, 0.5 mm
4 capillary, measurement time: 12 h) of the post TGA/DSC-material demonstrating that a mixture
5 of crystalline CoO (space group: $Fm\bar{3}m$; ICSD no. 9865),⁵⁶ $\text{Co}_3(\text{PO}_4)_2$ ($P2_1/c$, ICSD no. 4268),⁵⁷
6 and olivine-type LiCoPO_4 ($Pnma$, ICSD no. 431999)¹⁶ was formed upon heating. (c) Proposed
7 thermal decomposition process and theoretically expected weight fractions (in wt%) of the
8 involved phases. It can be inferred that the DSC signals and the weight loss observed in the TGA
9 (a) are correlated with the release of water (dehydration) and oxygen (oxidation of oxide ions) as
10 a result of a redox reaction.
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

26 CONCLUSION

27
28
29 A novel metastable, lithium-stabilized heterovalent cobalt (II,III) hydroxyl phosphate
30 framework with the empirical formula $\text{Co}_{0.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ and the structure-chemical formula
31 $\text{Co}_{11.0(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ was prepared by hydrothermal synthesis. The synthesis
32 conditions, the crystal structure, and material properties were discussed.
33
34
35
36
37

38
39 The pH value was identified as a key parameter of the hydrothermal process, and the phase pure
40 $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ -type material is exclusively produced at an intermediate pH value of 5.0
41 ($x = 0.16(3)$). In contrast, $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ was formed in a more acidic medium
42 ($3.0 \leq \text{pH} \leq 4.5$), whereas olivine-type LiCoPO_4 was obtained under alkaline conditions
43 ($\text{pH} = 8.0$). The uniform crystals of the material exhibit a unique triangular pyramid morphology
44 (dimensions: $15 \mu\text{m} \times 30 \mu\text{m}$) with a nanosheet-like primary structure. The trigonal phase (space
45 group: $P31m$, $a = 11.2533(4) \text{ \AA}$, $c = 4.9945(2) \text{ \AA}$, $V = 547.75(3) \text{ \AA}^3$, $Z = 1$) is isostructural with
46 natural phosphate minerals (satterlyite, holtedahlite) and features a partial Li substitution on the
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 Co sites. First experiments suggested that the Li substitution is crucial for the stabilization of the
4 structure since the synthesis of a Li-free $P31m$ -type $\text{Co}_2(\text{OH})\text{PO}_4$ framework proved unsuccessful.
5
6 The prevailing structural motif are double chains along the [001] direction, which are built from
7
8 $[\text{M}_2\text{O}_8(\text{OH})]$ ($M = \text{Co}, \text{Li}$) dimers and interconnected by tetrahedral $[\text{PO}_4]$ and $[\text{PO}_3\text{OH}]$ groups.
9
10 Whereas the occurrence of the OH groups was confirmed by infrared spectroscopy, X-ray
11 absorption spectroscopy studies revealed that the framework features mixed-valent Co ions
12
13 $(+2/+3)$, the occurrence of Co^{3+} likely being the result of the Li^+ substitution in order to obtain a
14 charge-balanced framework. Magnetic measurements demonstrated a paramagnetic to
15
16 antiferromagnetic transition at $T = 25$ K and a spin-glass-like behavior with a blocking temperature
17
18 of around 9 K. The metastable character of the mixed-valent framework was confirmed by
19
20 thermogravimetric analysis and differential scanning calorimetry. Driven by a redox reaction and
21
22 the intrinsic instability of Co^{3+} , the structure decomposes into CoO , $\text{Co}_3(\text{PO}_4)_2$, and LiCoPO_4 in a
23
24 two-step process, with the oxidation of oxide ions to oxygen being the first (558 °C, exothermic)
25
26 and the dehydration the second (633 °C, endothermic) step.
27
28
29
30
31
32
33
34
35

36 To conclude, this work provides fundamental insights into the synthesis and structure–property
37 relationships of cobalt hydroxide framework structures, and hence paves the way into modifying
38 the material properties for potential applications. Due to the occurrence of mixed-valent Co (II,III)
39 ions in the hydroxide–hydrogen phosphate–phosphate framework, it may act as a good oxygen-
40 evolving catalyst (OEC; *e.g.* for water splitting), similarly to the cobalt–phosphate (Co–Pi)
41 catalyst.⁵⁻⁷ As first experiments revealed that the solid solutions $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ ($x = 0.15(1)$ –
42
43 $0.35(3)$; refined from X-ray data) can be prepared, with the Li content increasing with the pH value
44
45 of the reaction mixture, future studies should focus onto compositional tuning of the material (*e.g.*
46
47 by varying the stoichiometry of the starting materials), which might be of significance for its
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 possible application in catalytic processes. In that context, the destabilizing effect of Co^{3+} as well
4
5 as the charge ordering of the $\text{Li}^+/\text{Co}^{2+}/\text{Co}^{3+}$ ions in the structure should be examined. Furthermore,
6
7 the synthesis of a non-Li-containing, $\text{Co}_2(\text{OH})\text{PO}_4$ *P31m*-type cobalt(II) framework should be
8
9 pursued. In order to completely resolve the structure, the proton distribution has to be determined
10
11 with respect to the H positions, degree of saturation, and a possible delocalization. Since the
12
13 formation of $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ as a side product of the hydrothermal synthesis of the olivine-type
14
15 cathode material LiCoPO_4 (*Pnma*) was revealed, it will be interesting to explore whether the
16
17 isostructural homologues $M_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ ($M = \text{Fe}, \text{Mn}, \text{Ni}$) exist and hence, also represent side
18
19 products of the respective hydrothermal synthesis processes towards the cathode materials LiMPO_4
20
21 ($M = \text{Fe}, \text{Mn}, \text{Ni}$).

22
23
24
25
26
27
28
29 ASSOCIATED CONTENT. **Supporting Information.** The following material is available free
30
31 of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.xxxxxxx:
32
33
34 1. Comparison of the PXRD pattern and lattice parameters with satterlyite and holtedahllite;
35
36 2. SEM and EDS; 3. IR spectrum; 4. Rietveld refinements of the PXRD patterns of the samples
37
38 obtained from hydrothermal syntheses in a pH range of 3.0–8.0; 5. Additional XAS data;
39
40 6. Additional magnetic data; 7. Rietveld refinement of the PXRD pattern of the post-TGA/DSC
41
42 material (PDF).
43
44

45
46
47 CCDC 1544992, 1544996–1545001, and 1545128–1545137 contain the supplementary
48
49 crystallographic data for this paper. The data can be obtained free of charge from The Cambridge
50
51 Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. Alternatively, the cif files may
52
53 also be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (e-mail:
54
55 crysdata@fiz-karlsruhe.de), on quoting the CSD numbers 432907–432923.
56
57
58
59
60

1
2
3 AUTHOR INFORMATION
45
6 **Corresponding Authors**
78
9 * E-mail: jennifer.ludwig@tum.de and tom.nilges@lrz.tum.de, Tel.: +49 89 289 13110,
1011 Fax: +49 89 289 13762
1213
14 **Author Contributions**
1516
17 J. L. conceived and designed this work, and carried out the synthesis, material characterization
18 (PXRD, IR, SEM/EDS), and data analysis (under the supervision of M. M. D. and T. N.). S. G.
19 and D. N. performed and analyzed magnetic and XAS measurements, respectively. J. L. wrote the
20 manuscript. All the authors approved the final version of this manuscript.
21
22
23
24
25
2627
28 **Funding Sources**
2930 This work has been funded by the Fonds der Chemischen Industrie and the TUM Graduate School.
31
32 The soft XAS experiments were performed at SSRL (Stanford Synchrotron Radiation
33 Lightsource), a Directorate of SLAC National Accelerator Laboratory supported by the US
34 Department of Energy, Office of Science, and Office of Basic Energy Sciences under contract
35 number DE-AC02-76SF00515.
36
37
38
39
40
41
4243
44 **ACKNOWLEDGMENT**
4546 The authors would like to thank P. Madhikar for TGA/DSC measurements, and U. Ammari for
47 elemental analysis. The help of C. Denk with a part of the syntheses is gratefully acknowledged.
48
49 J. Ludwig thanks the Fonds der Chemischen Industrie and the TUM Graduate School for financial
50 support of her Ph.D. project.
51
52
53
54
55
56
57
58
59
60

1
2
3 ABBREVIATIONS
4

5 AAS, atomic absorption spectroscopy; AC, alternating current; AEY, Auger electron yield; CN,
6 coordination number; DC, direct current; DSC, differential scanning calorimetry; EDS, energy-
7 dispersive X-ray spectroscopy; FC, field-cooled; IR, infrared; FY, fluorescence yield; HS, high-
8 spin; HT, hydrothermal; ICSD, Inorganic Crystal Structure Database; OEC, oxygen-evolving
9 catalyst; OER, oxygen evolution reaction; PSD, position-sensitive detector; PTFE,
10 poly(tetrafluoroethylene); PXRD, powder X-ray diffraction; SEM, scanning electron microscope;
11 SQUID, superconducting quantum interference device; TEY, total electron yield; TFM,
12 perfluoro(propylvinylether)-modified PTFE; TGA, thermogravimetric analysis; XAS, X-ray
13 absorption spectroscopy; ZFC, zero-field-cooled.
14
15
16
17
18
19
20
21
22
23
24
25
26

27 REFERENCES
28

- 29
30 (1) MasPOCH, D.; Ruiz-Molina, D.; Veciana, J., Old materials with new tricks: multifunctional
31 open-framework materials. *Chem. Soc. Rev.* **2007**, 36, (5), 770-818.
32
33 (2) Hogarth, C. A.; Jamel Basha, M., Electrical conduction in cobalt-phosphate glasses. *J.*
34 *Phys. D* **1983**, 16, (5), 869-878.
35
36 (3) Anderson, M. T.; Phillips, M. L. F.; Sinclair, M. B.; Stucky, G. D., Synthesis of Transition-
37 Metal-Doped KTiOPO₄ and Lanthanide-Doped RbTiOAsO₄ Isomorphs That Absorb Visible
38 Light. *Chem. Mater.* **1996**, 8, (1), 248-256.
39
40 (4) Millet, J.-M. M., FePO catalysts for the selective oxidative dehydrogenation of isobutyric
41 acid into methacrylic acid. *Catal. Rev. - Sci. Eng.* **1998**, 40, (1 & 2), 1-38.
42
43 (5) Kanan, M. W.; Nocera, D. G., In Situ Formation of an Oxygen-Evolving Catalyst in
44 Neutral Water Containing Phosphate and Co²⁺. *Science* **2008**, 321, (5892), 1072-1075.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (6) Kanan, M. W.; Surendranath, Y.; Nocera, D. G., Cobalt-phosphate oxygen-evolving
4 compound. *Chem. Soc. Rev.* **2009**, 38, (1), 109-114.
5
6
7
8 (7) Zhong, D. K.; Gamelin, D. R., Photoelectrochemical Water Oxidation by Cobalt Catalyst
9 ("Co-Pi")/ α -Fe₂O₃ Composite Photoanodes: Oxygen Evolution and Resolution of a Kinetic
10 Bottleneck. *J. Am. Chem. Soc.* **2010**, 132, (12), 4202-4207.
11
12
13
14 (8) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B., Phospho-olivines as Positive-
15 Electrode Materials for Rechargeable Lithium Batteries. *J. Electrochem. Soc.* **1997**, 144, (4), 1188-
16 1194.
17
18
19
20
21 (9) Amine, K.; Yasuda, H.; Yamachi, M., Olivine LiCoPO₄ as 4.8 V electrode material for
22 lithium batteries. *Electrochem. Solid-State Lett.* **2000**, 3, (4), 178-179.
23
24
25
26 (10) Zaghbi, K.; Guerfi, A.; Hovington, P.; Vijh, A.; Trudeau, M.; Mauger, A.; Goodenough, J.
27 B.; Julien, C. M., Review and analysis of nanostructured olivine-based lithium rechargeable
28 batteries: Status and trends. *J. Power Sources* **2013**, 232, 357-369.
29
30
31
32 (11) Masquelier, C.; Croguennec, L., Polyanionic (phosphates, silicates, sulfates) frameworks
33 as electrode materials for rechargeable Li (or Na) batteries. *Chem. Rev.* **2013**, 113, (8), 6552-6591.
34
35
36 (12) Abrahams, S. C.; Bernstein, J. L., Crystal structure of paramagnetic ludlamite,
37 Fe₃(PO₄)₂·4H₂O, at 298°K. *J. Chem. Phys.* **1966**, 44, (6), 2223-2229.
38
39
40
41 (13) Rabenau, A., The role of hydrothermal synthesis in preparative chemistry. *Angew. Chem.*
42 **1985**, 97, (12), 1017-1032.
43
44
45 (14) Ludwig, J.; Marino, C.; Haering, D.; Stinner, C.; Nordlund, D.; Doeff, M. M.; Gasteiger,
46 H. A.; Nilges, T., Facile, ethylene glycol-promoted microwave-assisted solvothermal synthesis of
47 high-performance LiCoPO₄ as a high-voltage cathode material for lithium-ion batteries. *RSC Adv.*
48 **2016**, 6, 82984-82994.
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (15) Ludwig, J.; Haering, D.; Doeff, M. M.; Nilges, T., Particle size-controllable microwave-assisted solvothermal synthesis of the high-voltage cathode material LiCoPO₄ using water/ethylene glycol solvent blends. *Solid State Sci.* **2017**, *65*, 100-109.
- (16) Ludwig, J.; Marino, C.; Haering, D.; Stinner, C.; Gasteiger, H. A.; Nilges, T., Morphology-controlled microwave-assisted solvothermal synthesis of high-performance LiCoPO₄ as a high-voltage cathode material for Li-ion batteries. *J. Power Sources* **2017**, *342*, 214-223.
- (17) Rivera, J. P., The linear magnetoelectric effect in LiCoPO₄ revisited. *Ferroelectrics* **1994**, *161*, (1-4), 147-164.
- (18) Kharchenko, N. F.; Kharchenko, Y. N.; Szymczak, R.; Baran, M.; Schmid, H., Weak ferromagnetism in the antiferromagnetic magnetoelectric crystal LiCoPO₄. *Low Temp. Phys.* **2001**, *27*, (9-10), 895-898.
- (19) Harrison, W. T. A.; Vaughey, J. T.; Dussack, L. L.; Jacobson, A. J.; Martin, T. E.; Stucky, G. D., Two new adamite-type phases, Co₂(OH)PO₄ and Zn₂(OH)PO₄: structure-directing effect of organic additives. *J. Solid State Chem.* **1995**, *114*, (1), 151-158.
- (20) Wang, G.; Valldor, M.; Spielberg, E. T.; Mudring, A.-V., Ionothermal Synthesis, Crystal Structure, and Magnetic Study of Co₂PO₄OH Isostructural with Caminite. *Inorg. Chem.* **2014**, *53*, (6), 3072-3077.
- (21) Kokkoros, P., The structure of adamite. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1937**, *96*, 417-434.
- (22) Hill, R. J., The crystal structure and infrared properties of adamite. *Am. Mineral.* **1976**, *61*, (9-10), 979-986.
- (23) Rojo, J. M.; Mesa, J. L.; Lezama, L.; Pizarro, J. L.; Arriortua, M. I.; Fernandez, J. R.; Barberis, G. E.; Rojo, T., Spin-glass behavior in a three-dimensional antiferromagnet ordered

1
2
3 phase: Magnetic structure of $\text{Co}_2(\text{OH})(\text{PO}_4)$. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**,
4
5
6 66, (9), 094406/1-094406/13.

7
8 (24) de Pedro, I.; Rojo, J. M.; Jubera, V.; Fernandez, J. R.; Marcos, J. S.; Lezama, L.; Rojo, T.,
9
10 Effect of Ni^{2+} ($S = 1$) and Cu^{2+} ($S = 1/2$) substitution on the antiferromagnetic ordered phase
11
12 $\text{Co}_2(\text{OH})\text{PO}_4$ with spin glass behavior. *J. Mater. Chem.* **2004**, 14, (7), 1157-1163.

13
14 (25) de Pedro, I.; Jubera, V.; Rojo, J. M.; Lezama, L.; Sanchez Marcos, J.; Rodriguez
15
16 Fernandez, J.; Mesa, J. L.; Rojo, T.; Arriortua, M. I., Magnetic properties of $\text{Co}_{2-x}\text{Cu}_x(\text{OH})\text{PO}_4$
17
18 ($x=0, 1$ and 2). *J. Magn. Magn. Mater.* **2004**, 272-276, (Suppl. 1), E665-E666.

19
20 (26) de Pedro, I.; Rojo, J. M.; Lezama, L.; Rojo, T., Spectroscopic and magnetic properties of
21
22 $\text{Co}_{1.7}\text{Mn}_{0.3}(\text{OH})\text{PO}_4$. *Z. Anorg. Allg. Chem.* **2007**, 633, (11-12), 1847-1852.

23
24 (27) de Pedro, I.; Rojo, J. M.; Rodriguez Fernandez, J.; Lezama, L.; Rojo, T., Synthesis,
25
26 Spectroscopic and Magnetic Properties of the $\text{Co}_2(\text{OH})(\text{PO}_4)_{1-x}(\text{AsO}_4)_x$ [$0 \leq x \leq 1$] Solid Solution.
27
28
29
30
31
32
33 *Eur. J. Inorg. Chem.* **2010**, (17), 2514-2522.

34 (28) Keefer, K. D.; Hochella, M. F., Jr.; De Jong, B. H. W. S., The structure of the magnesium
35
36 hydroxide sulfate hydrate $\text{MgSO}_4 \cdot 1/3\text{Mg}(\text{OH})_2 \cdot 1/3\text{H}_2\text{O}$. *Acta Crystallogr., Sect. B* **1981**, B37, (5),
37
38 1003-1006.

39
40 (29) Gheith, M. A., Lipscombite: a new synthetic "iron lazulite.". *Am. Mineral.* **1953**, 38, 612-
41
42 628.

43
44 (30) Mandarino, J. A.; Sturman, B. D.; Corlett, M. I., Satterlyite, a new hydroxyl-bearing
45
46 ferrous phosphate from the Big Fish River area, Yukon Territory [Canada]. *Can. Mineral.* **1978**,
47
48 16, (3), 411-413.

49
50 (31) Kolitsch, U.; Andrut, M.; Giester, G., Satterlyite, $(\text{Fe,Mg})_{12}(\text{PO}_3\text{OH})(\text{PO}_4)_5(\text{OH},\text{O})_6$:
51
52
53
54
55
56
57
58
59
60 crystal structure and infrared absorption spectra. *Eur. J. Mineral.* **2002**, 14, (1), 127-133.

- 1
2
3 (32) Raade, G.; Mladeck, M. H., Holtedahlite, a new magnesium phosphate from Modum,
4 Norway. *Lithos* **1979**, 12, (4), 283-287.
5
6
7
8 (33) Roemming, C.; Raade, G., The crystal structure of natural and synthetic holtedahlite.
9
10 *Mineral. Petrol.* **1989**, 40, (2), 91-100.
11
12 (34) Petricek, V.; Dusek, M.; Palatinus, L., Crystallographic Computing System JANA2006:
13 General features. *Z. Kristallogr. - Cryst. Mater.* **2014**, 229, (5), 345-352.
14
15
16 (35) Finger, L. W.; Cox, D. E.; Jephcoat, A. P., A correction for powder diffraction peak
17 asymmetry due to axial divergence. *J. Appl. Crystallogr.* **1994**, 27, (6), 892-900.
18
19
20 (36) Cromer, D. T.; Liberman, D. A., Anomalous dispersion calculations near to and on the
21 long-wavelength side of an absorption edge. *Acta Crystallogr., Sect. A* **1981**, A37, (2), 267-268.
22
23
24 (37) Gelato, L. M.; Parthe, E., STRUCTURE TIDY - a computer program to standardize crystal
25 structure data. *J. Appl. Cryst.* **1987**, 20, (2), 139-143.
26
27
28 (38) Spek, A. L., Structure validation in chemical crystallography. *Acta Crystallogr., Sect. D:*
29 *Biol. Crystallogr.* **2009**, 65, (2), 148-155.
30
31
32 (39) Berar, J. F.; Lelann, P., E.S.D.'s and estimated probable error obtained in Rietveld
33 refinements with local correlations. *J. Appl. Crystallogr.* **1991**, 24, (1), 1-5.
34
35
36 (40) Lin, F.; Nordlund, D.; Markus, I. M.; Weng, T.-C.; Xin, H. L.; Doeff, M. M., Profiling the
37 nanoscale gradient in stoichiometric layered cathode particles for lithium-ion batteries. *Energ.*
38 *Environ. Sci.* **2014**, 7, (9), 3077-3085.
39
40
41 (41) Hibberd, A. M.; Doan, H. Q.; Glass, E. N.; de Groot, F. M. F.; Hill, C. L.; Cuk, T., Co
42 Polyoxometalates and a Co₃O₄ Thin Film Investigated by L-Edge X-ray Absorption Spectroscopy.
43 *J. Phys. Chem. C* **2015**, 119, (8), 4173-4179.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

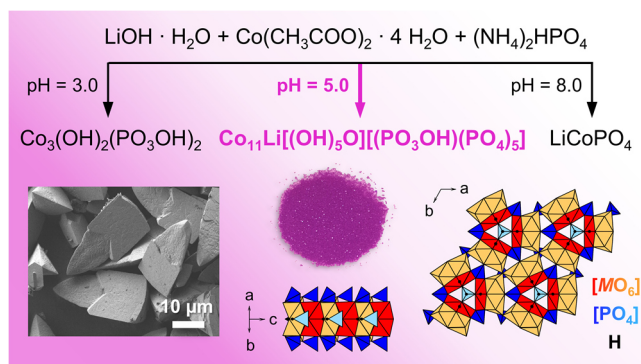
- 1
2
3 (42) Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic
4 distances in halides and chalcogenides. *Acta Crystallogr., Sect. A* **1976**, A32, (5), 751-767.
5
6
7
8 (43) Brunet, F.; Schaller, T., Protons in the magnesium phosphates phosphoellenbergerite and
9 holtedahlite: an IR and NMR study. *Am. Mineral.* **1996**, 81, (3-4), 385-394.
10
11
12 (44) Strobridge, F. C.; Clement, R. J.; Leskes, M.; Middlemiss, D. S.; Borkiewicz, O. J.;
13 Wiaderek, K. M.; Chapman, K. W.; Chupas, P. J.; Grey, C. P., Identifying the Structure of the
14 Intermediate, $\text{Li}_{2/3}\text{CoPO}_4$, Formed during Electrochemical Cycling of LiCoPO_4 . *Chem. Mater.*
15 **2014**, 26, (21), 6193-6205.
16
17
18 (45) Effenberger, H., Structure refinement of tricobalt dihydroxide bis(hydrogen phosphate)
19 and cobalt bis(dihydrogen phosphate) dihydrate. *Acta Crystallogr., Sect. C: Cryst. Struct.*
20 *Commun.* **1992**, C48, (12), 2104-2107.
21
22
23 (46) Marcos, M. D.; Amoros, P.; Beltran-Porter, A.; Martinez-Manez, R.; Attfield, J. P., Novel
24 crystalline microporous transition-metal phosphites $M_{11}(\text{HPO}_3)_8(\text{OH})_6$ ($M = \text{Zn}, \text{Co}, \text{Ni}$). X-ray
25 powder diffraction structure determination of the cobalt and nickel derivatives. *Chem. Mater.*
26 **1993**, 5, (1), 121-128.
27
28
29 (47) Haynes, W. M., Dissociation Constants of Inorganic Acids and Bases In *CRC Handbook of*
30 *Chemistry and Physics*, 94th ed.; CRC Press: Boca Raton, FL, 2013; pp 5-92.
31
32
33 (48) Huang, X.; Ma, J.; Wu, P.; Hu, Y.; Dai, J.; Zhu, Z.; Chen, H.; Wang, H., Hydrothermal
34 synthesis of LiCoPO_4 cathode materials for rechargeable lithium-ion batteries. *Mater. Lett.* **2005**,
35 **59**, (5), 578-582.
36
37
38 (49) Vegard, L., Die Konstitution der Mischkristalle und die Raumfüllung der Atome. *Z. Physik*
39 **1921**, 5, (1), 17-26.
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

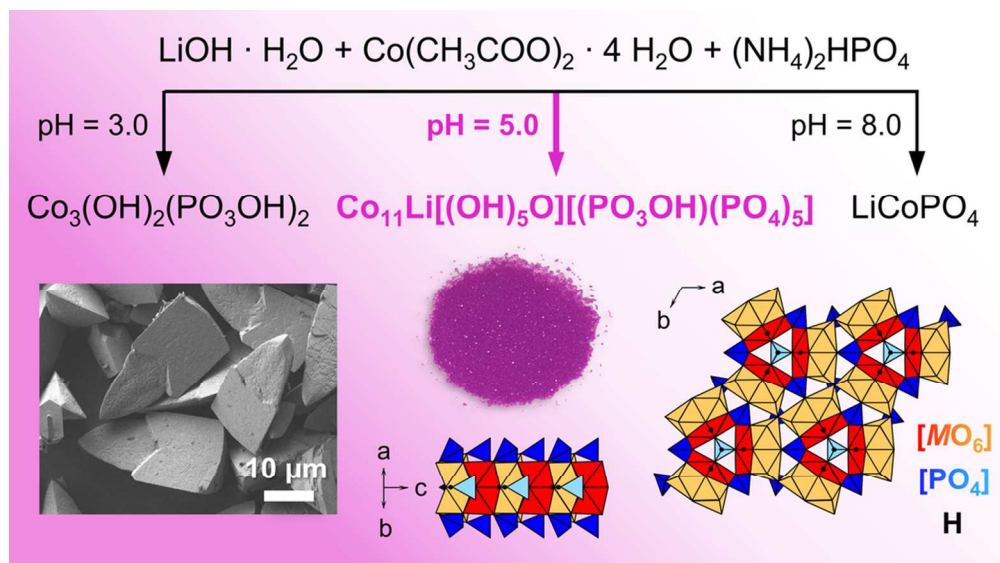
- 1
2
3 (50) Chen, J.; Vacchio, M. J.; Wang, S.; Chernova, N.; Zavalij, P. Y.; Whittingham, M. S., The
4 hydrothermal synthesis and characterization of olivines and related compounds for
5 electrochemical applications. *Solid State Ion.* **2008**, 178, (31-32), 1676-1693.
6
7
8
9
10 (51) Jaehne, C.; Neef, C.; Koo, C.; Meyer, H.-P.; Klingeler, R., A new LiCoPO₄ polymorph via
11 low temperature synthesis. *J. Mater. Chem. A* **2013**, 1, (8), 2856-2862.
12
13
14 (52) Wu, B.; Xu, H.; Mu, D.; Shi, L.; Jiang, B.; Gai, L.; Wang, L.; Liu, Q.; Ben, L.; Wu, F.,
15 Controlled solvothermal synthesis and electrochemical performance of LiCoPO₄ submicron single
16 crystals as a cathode material for lithium ion batteries. *J. Power Sources* **2016**, 304, 181-188.
17
18
19
20 (53) de Groot, F. M. F.; Abbate, M.; van Elp, J.; Sawatzky, G. A.; Ma, Y. J.; Chen, C. T.; Sette,
21 F., Oxygen 1s and cobalt 2p x-ray absorption of cobalt oxides. *J. Phys.: Condens. Matter* **1993**, 5,
22 (14), 2277-2288.
23
24
25
26
27 (54) de Groot, F. M. F.; Fuggle, J. C.; Thole, B. T.; Sawatzky, G. A., The 2p x-ray absorption
28 of 3d transition-metal compounds: an atomic multiplet description including the crystal field. *Phys.*
29 *Rev. B: Condens. Matter* **1990**, 42, (9), 5459-5468.
30
31
32
33 (55) Hu, Z.; Wu, H.; Haverkort, M. W.; Hsieh, H. H.; Lin, H. J.; Lorenz, T.; Baier, J.; Reichl,
34 A.; Bonn, I.; Felser, C.; Tanaka, A.; Chen, C. T.; Tjeng, L. H., Different Look at the Spin State of
35 Co³⁺ Ions in a CoO₅ Pyramidal Coordination. *Phys. Rev. Lett.* **2004**, 92, (20), 207402/1-207402/4.
36
37
38 (56) Sasaki, S.; Fujino, K.; Takeuchi, Y., X-ray determination of electron-density distributions
39 in oxides, magnesium oxide, manganese(II) oxide, cobalt oxide, and nickel(II) oxide, and atomic
40 scattering factors of their constituent atoms. *Proc. Jpn. Acad., Ser. B* **1979**, 55, (2), 43-48.
41
42
43 (57) Anderson, J. B.; Kostiner, E.; Miller, M. C.; Rea, J. R., Crystal structure of cobalt
44 orthophosphate Co₃(PO₄)₂. *J. Solid State Chem.* **1975**, 14, (4), 372-377.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Table of Contents Only

1
2
3
4
5
6
7 SYNOPSIS. A new metastable compound, featuring a lithium-stabilized mixed-valent cobalt
8
9 (II,III) hydroxide phosphate framework, $\text{Co}_{11.0(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ (space group:
10
11 $P31m$, $Z = 1$, simplified composition: $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$), was prepared by hydrothermal
12
13 synthesis. The dominant structural feature are alternating double chains of $[\text{M}_2\text{O}_8(\text{OH})]$ ($M = \text{Co}$,
14
15 Li) dimer units, which run along the $[001]$ direction and are connected via $[\text{PO}_4]$ and $[\text{PO}_3(\text{OH})]$
16
17 tetrahedra. The synthesis conditions, crystal structure, and physical properties of the material are
18
19 tetrahedra. The synthesis conditions, crystal structure, and physical properties of the material are
20
21 discussed.
22
23

TOC GRAPHIC





26 A new metastable compound, featuring a lithium-stabilized mixed-valent cobalt (II,III) hydroxide phosphate
 27 framework, $\text{Co}_{11.0(1)}\text{Li}_{1.0(2)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ (space group: $P31m$, $Z = 1$, simplified composition:
 28 $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$), was prepared by hydrothermal synthesis. The dominant structural feature are
 29 alternating double chains of $[\text{M}_2\text{O}_8(\text{OH})]$ ($M = \text{Co}, \text{Li}$) dimer units, which run along the $[001]$ direction and
 30 are connected via $[\text{PO}_4]$ and $[\text{PO}_3(\text{OH})]$ tetrahedra. The synthesis conditions, crystal structure, and physical
 31 properties of the material are discussed.

32 47x26mm (600 x 600 DPI)

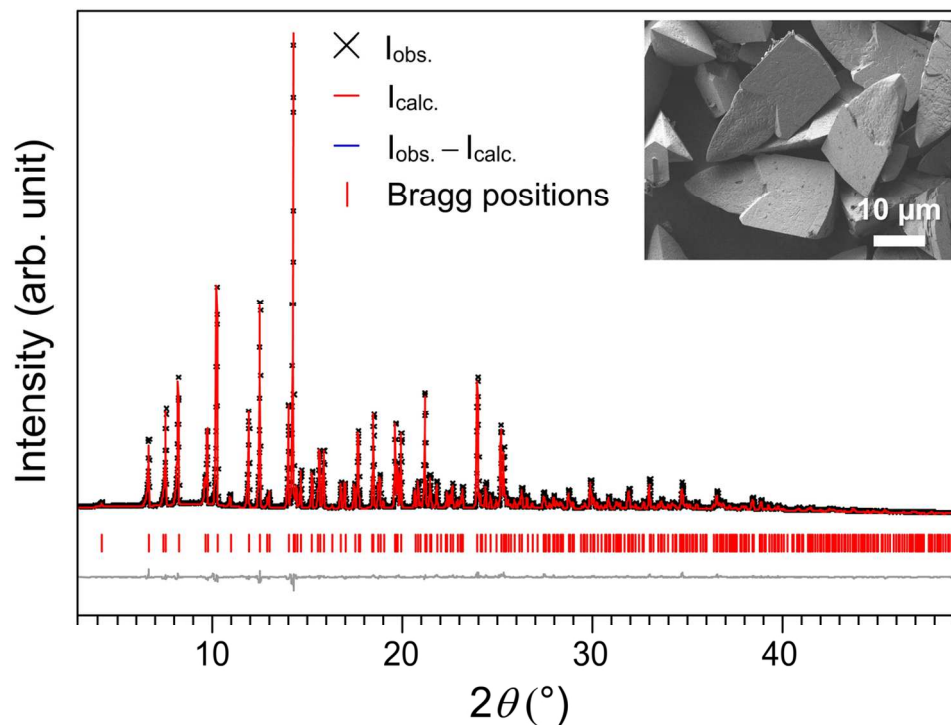


Figure 1. Rietveld fit of the powder X-ray diffraction data (Mo $K_{\alpha 1}$ radiation, 0.5 mm capillary, measurement time: 12 h) of $\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$ (crystal-chemical formula: $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$, space group: $P31m$, $Z = 1$) prepared by the hydrothermal process at pH = 5.0. Inset: Scanning electron microscopy image demonstrating that the sample consists of uniform, well-dispersed crystals with an elongated triangular pyramid morphology and dimensions of $\sim 15 \mu\text{m} \times 30 \mu\text{m}$.

63x47mm (600 x 600 DPI)

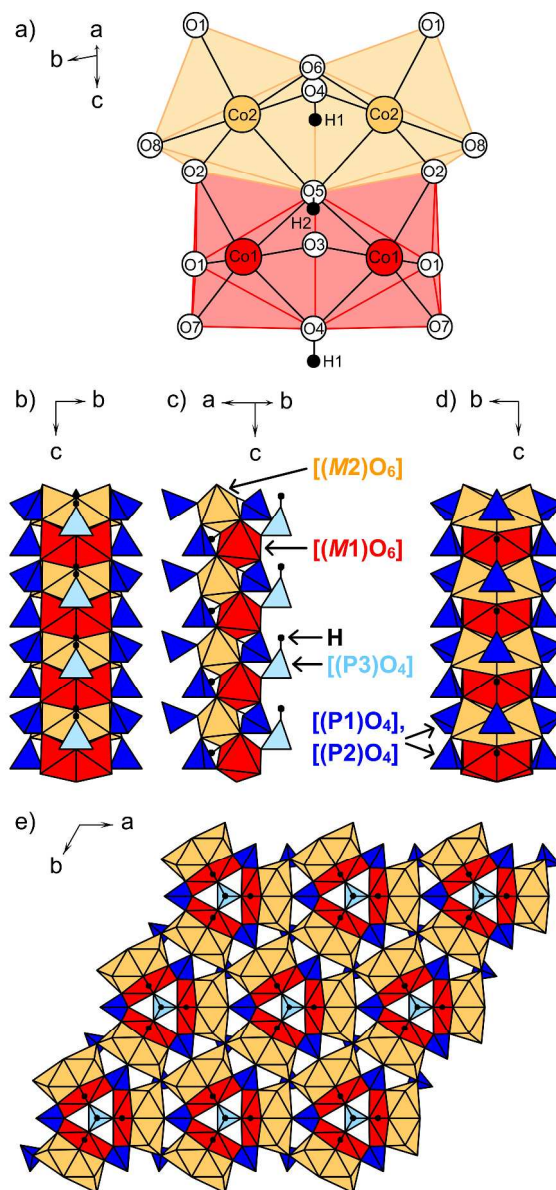


Figure 2. Polyhedral representation of the crystal structure of $\text{Co}_{11.1(1)}\text{Li}_{0.9(1)}[(\text{OH})_5\text{O}][(\text{PO}_3\text{OH})(\text{PO}_4)_5]$ (space group: $P31m$, $Z = 1$; simplified formula: $\text{Co}_{1.85(1)}\text{Li}_{0.15(1)}(\text{OH})\text{PO}_4$). (a) The structure features two independent M ($M = \text{Co}, \text{Li}$) sites, $M1$ (red; populations: 97.1(8)% Co, 2.9(8)% Li) and $M2$ (orange; 87.8(8)% Co, 12.2(8)% Li), which are coordinated by O atoms (white) in an octahedral geometry. The $[(M1)\text{O}_6]$ (red) and $[(M2)\text{O}_6]$ (orange) units form face-sharing $[(M1)_2\text{O}_8(\text{OH})]$ and $[(M2)_2\text{O}_8(\text{OH})]$ dimers with μ_2 -bridging OH groups (H: black; occupancy: 83.3%). (b–d) Through edge-sharing of the dimers along $[001]$, alternating double chains are formed (viewed along different directions), which represent the dominant structural motif. (e) The double chains are further connected by three different, tetrahedral $[\text{PO}_4]$ units to form a three-dimensional network in which each double chain shares corners with six other double chains. Whereas the $[(P1)\text{O}_4]$ and $[(P2)\text{O}_4]$ tetrahedra (dark blue) share all apical O atoms with the network, the $[(P3)\text{O}_3(\text{OH})]$ group (light blue) only contributes three O atoms.

178x376mm (600 x 600 DPI)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

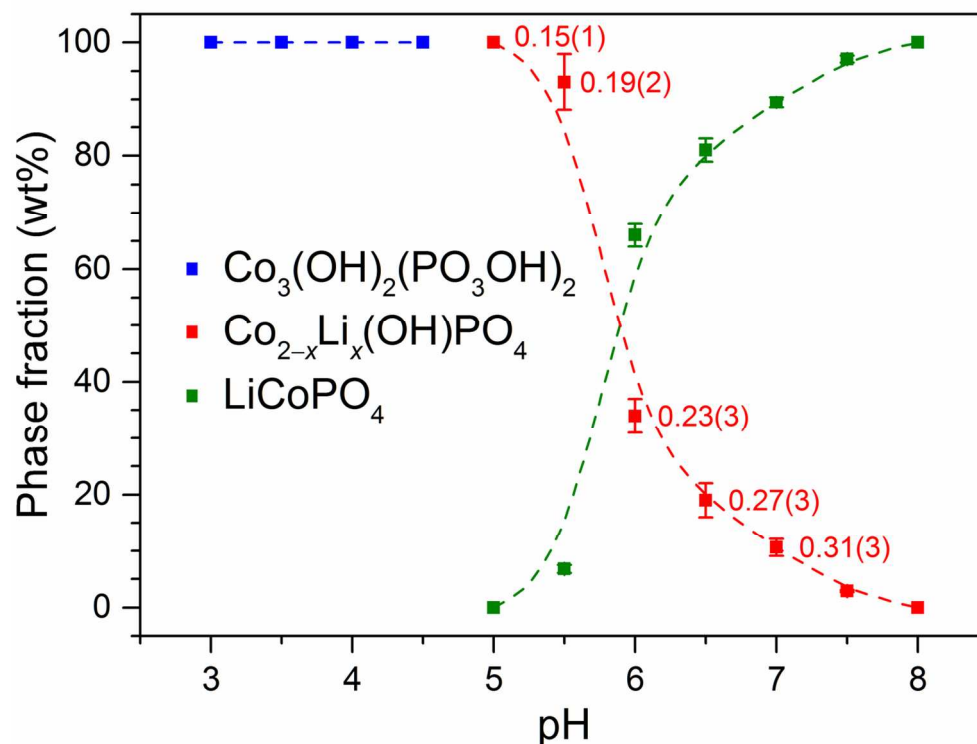


Figure 3. Phase fractions (in wt%; obtained from multi-component Rietveld refinements) versus pH value of the reaction mixture demonstrating that the formation of the phases $\text{Co}_3(\text{OH})_2(\text{PO}_3\text{OH})_2$ (space group: $P2_1/c$), $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ ($P31m$; the refined Li contents x are displayed in red along the data points for pH = 5.0–7.0 with standard deviations in parentheses), and LiCoPO_4 ($Pnma$) from the hydrothermal process is extremely pH-sensitive. It is evident that a pure $\text{Co}_{2-x}\text{Li}_x(\text{OH})\text{PO}_4$ -type material is only realized at pH = 5.0. Non-visible error bars are smaller than the data points. Data points not shown correspond to a phase fraction of 0 wt%, meaning that no reflections of the respective phases were detected in the PXRD pattern.

63x47mm (600 x 600 DPI)

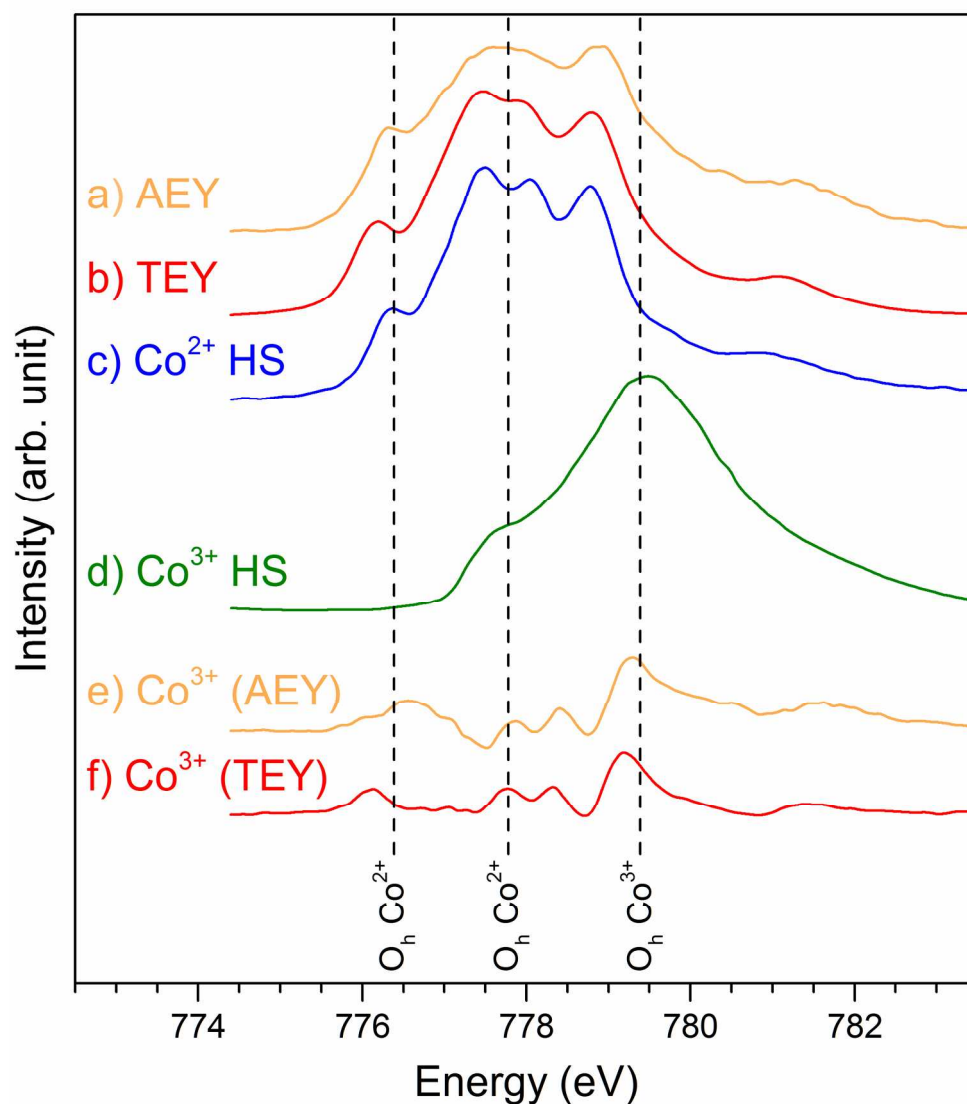


Figure 4. Normalized Co L_{3} -edge XAS spectra of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ (prepared by hydrothermal synthesis at $\text{pH} = 5.0$) in the (a) AEY (orange) and (b) TEY (red) modes compared to reference spectra for octahedrally (O_h) coordinated (c) high-spin (HS) Co^{2+} (blue; CoO , adapted from ref. ⁴⁵), and (d) high-spin (HS) Co^{3+} (green; $\text{Sr}_2\text{CoO}_3\text{Cl}$, adapted from ref. ⁵⁹). (e) and (f) show the difference spectra resulting from the subtraction of 15% and 6% Co^{2+} from the AEY and TEY spectra of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$, respectively, which represents the Co^{3+} contributions. The increased Co^{3+} contribution at the top surface (AEY, *cf.* a,e) compared to the bulk (TEY; *cf.* b,f) of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ is evident. All datasets have been aligned to match the common energy scale of reference ⁴⁵. The vertical dashed lines indicate the energies corresponding to $\text{O}_h \text{Co}^{2+}$ (characteristic shoulder: 776.4 eV; doublet: 777.7 eV) as well $\text{O}_h \text{Co}^{3+}$ (779.4 eV).

93x104mm (600 x 600 DPI)

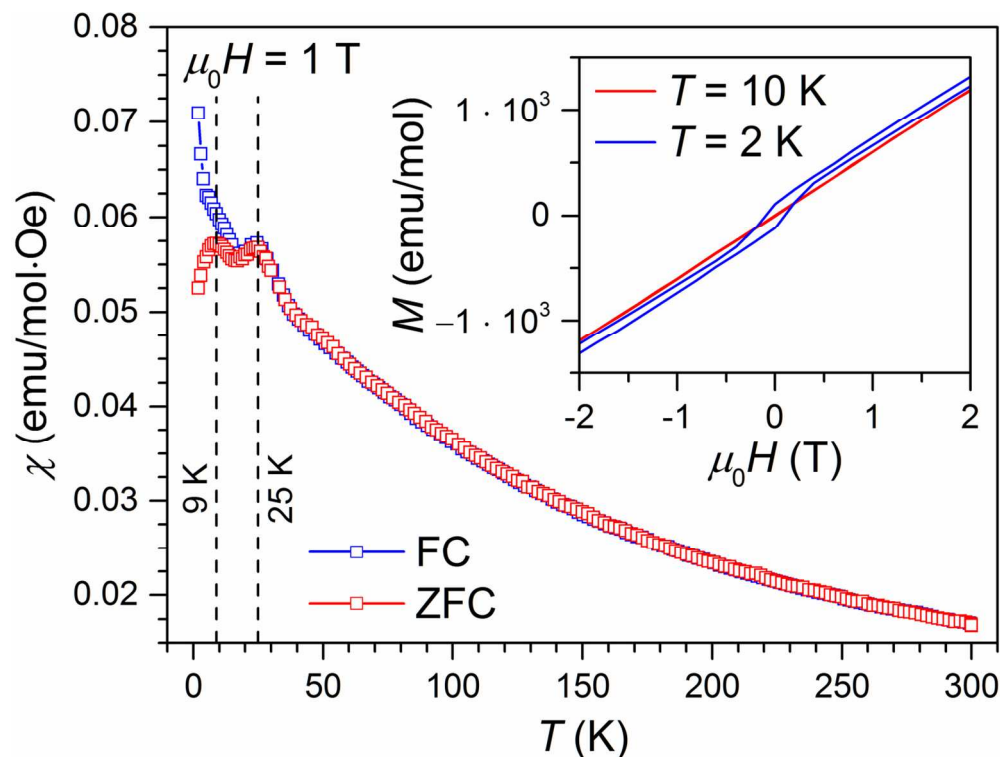


Figure 5. Magnetic susceptibility of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ (prepared by hydrothermal synthesis at pH = 5.0) as a function of temperature measured at a magnetic field of 1 T under field-cooled (FC) and zero-field-cooled (ZFC) conditions. The vertical dashed lines indicate the temperature of the paramagnetic to antiferromagnetic transition (25 K) as well as the blocking temperature of the spin-glass-like behavior (9 K) at low temperature. Inset: Magnetic hysteresis curves measured at temperatures of $T = 10$ K and 2 K, respectively.

63x47mm (600 x 600 DPI)

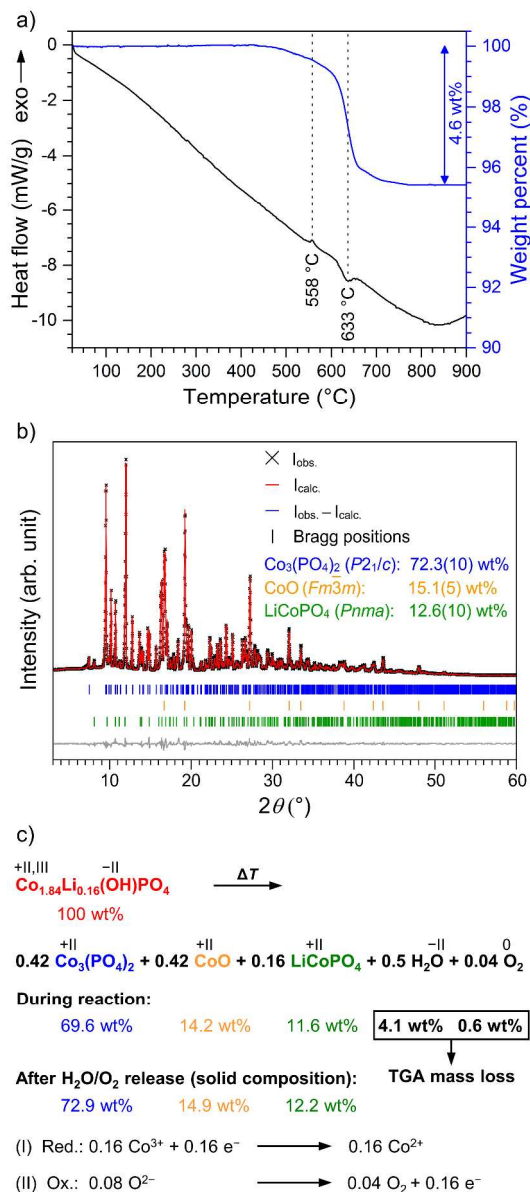


Figure 6. (a) DSC (black) and TGA (blue) curves of $\text{Co}_{1.84(2)}\text{Li}_{0.16(3)}(\text{OH})\text{PO}_4$ measured under Ar in a temperature range of 30–900 °C (heating rate: 10 °C·min⁻¹). Two DSC signals are observed at 558 °C (exothermic) and 633 °C (endothermic), which are accompanied by a total weight loss of 4.6 wt%. (b) Rietveld fit of the powder X-ray diffraction data (Mo $K_{\alpha 1}$ radiation, 0.5 mm capillary, measurement time: 12 h) of the post TGA/DSC-material demonstrating that a mixture of crystalline CoO (space group: $Fm\bar{3}m$; ICSD no. 9865),⁶⁴ $\text{Co}_3(\text{PO}_4)_2$ ($P2_1/c$, ICSD no. 4268),⁶⁵ and olivine-type LiCoPO_4 ($Pnma$, ICSD no. 431999)¹⁹ was formed upon heating. (c) Proposed thermal decomposition process and theoretically expected weight fractions (in wt%) of the involved phases. It can be inferred that the DSC signals and the weight loss observed in the TGA (a) are correlated with the release of water (dehydration) and oxygen (oxidation of oxide ions) as a result of a redox reaction.

192x440mm (600 x 600 DPI)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60