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Ionothermal Synthesis, Crystal Structure, and Magnetic Study of Co$_2$PO$_4$OH Isostructural with Caminite

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* Supporting Information

ABSTRACT: A new framework cobalt(II) hydroxyl phosphate, Co$_2$PO$_4$OH, was prepared by ionothermal synthesis using 1-butyl-4-methyl-pyridinium hexafluorophosphate as the ionic liquid. As the formation of Co$_2$PO$_4$F competes in the synthesis, the synthesis conditions have to be judiciously chosen to obtain well-crystallized, single phase Co$_2$PO$_4$OH. Single-crystal X-ray diffraction analyses reveal Co$_2$PO$_4$OH crystallizes with space group I4$_1$/amd (a = b = 5.2713(7) Å, c = 12.907(3) Å, V = 358.63(10) Å$^3$, and Z = 4). Astonishingly, it does not crystallize isotypically with Co$_2$PO$_4$F but rather isotypically with the hydroxyl minerals caminite Mg$_{1.33}$[SO$_4$(OH)$_{0.66}$(H$_2$O)$_{0.33}$] and lipscombite Fe$_2$(PO$_4$(OH) (0 < y ≤ 2/3). Phosphate tetrahedra groups interconnect four rod-packed face-sharing $\lfloor$Co$_{12}O_{36}\rceil$ octahedra chains to form a three-dimensional framework structure. The compound Co$_2$PO$_4$OH was further characterized by powder X-ray diffraction, Fourier transform–infrared, and ultraviolet–visible spectroscopy, confirming the discussed structure. The magnetic measurement reveals that Co$_2$PO$_4$OH undergoes a magnetic transition and presents at low temperatures a canted antiferromagnetic spin order in the ground state.

INTRODUCTION

Phosphorus is the 10th most abundant element on earth and tends to be concentrated in igneous rocks.² Naturally occurring phosphate minerals have rich crystal chemistry; the major constituents of phosphorite are the minerals of the apatite group.³ A large number of structurally and chemically diverse synthetic metallophosphates⁴ are extensively studied with respect to a wide range of applications, such as ion exchange,⁵ catalysis,⁶ adsorption,⁷ nonlinear optics,⁸ and battery materials.⁹ Since cobalt phosphate was used as a component in semiconductive glasses,⁹ such materials have attracted renewed interest in the field of ion-selective microelectrodes, catalysts, battery electrodes, and glass materials.¹⁰ Furthermore, cobalt phosphate has been studied as a solid-state catalyst in the solar light-induced oxidation of water to O$_2$.¹⁰c Current cobalt phosphates are being extensively studied as cathode materials for rechargeable lithium ion batteries to increase energy storage and voltage output.¹⁰c

In the field of open-framework metallophosphates, cobalt phosphates are of particular interest as Co$^{2+}$ is one of the few transition-metal cations that not only can adopt an octahedral but also a tetrahedral coordination environment and thus is able to substitute silicon or phosphorus in silicates and phosphates. The incorporation of cobalt cations into zeolites can improve the catalytic performance of the material.¹¹ In addition, cobalt phosphates are of interest because of their magnetic properties.¹² Since the first amino-templated tetrahedral open framework cobalt phosphate [C$_2$H$_{10}$N$_2$]$_2$[CoPO$_4$] was reported in 1994, much attention has been paid to this class of compounds.¹³ Recent, our group successfully utilized ionic liquids (ILs) in the synthesis of metal, metal fluoride, and metal oxide nanomaterials for energy-related applications, for example, in catalysis or photonic materials.¹⁴ At the same time, we have explored a wide range of ILs with different cations and anions in the synthesis of layered and framework aluminophosphates,¹⁵ a new aluminum fluoride hexahydrate, a new open-framework iron borophosphate,¹⁶ and a manganese borophosphate, KMnP$_2$O$_7$(OH)$_2$.¹⁷ The advantage of tetrafluoroborate or hexafluorophosphate ionic liquids in the synthesis of metal phosphates is that such ionic liquids can not only serve as the solvent and template but also as the mineralizer, because of the release of fluoride anions during the reaction.

We describe herein how this process can be used to prepare, by a judicious choice of the reaction parameters, highly crystalline single-phased Co$_2$PO$_4$OH, whose magnetic susceptibility will be described.

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Table 1. Details of Initial Mixture and Crystallization Conditions for the Preparation of Co2PO4OH

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>T (°C)</th>
<th>t (d)</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Co(OAc)2·4H2O·H3PO4·0.75H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1)</td>
</tr>
<tr>
<td>S2</td>
<td>Co(OAc)2·4H2O·H3PO4·0.75H3BO3·0.5[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1) + (2)</td>
</tr>
<tr>
<td>S3</td>
<td>Co(OAc)2·4H2O·H3PO4·0.75H3BO3·0.25[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>unknown phase</td>
</tr>
<tr>
<td>S4</td>
<td>Co(OAc)2·4H2O·H3PO4·0.75H3BO3·2[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1) + amorphous</td>
</tr>
<tr>
<td></td>
<td>different amount of Co(OAc)2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>1.2Co(OAc)2·4H2O·H3PO4·0.75H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1) + (2)</td>
</tr>
<tr>
<td>S6</td>
<td>1.8Co(OAc)2·4H2O·H3PO4·0.75H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(2) + (1)</td>
</tr>
<tr>
<td></td>
<td>different amount of H3BO3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>Co(OAc)2·4H2O·2H3PO4·H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1)</td>
</tr>
<tr>
<td>S8</td>
<td>Co(OAc)2·4H2O·(2/3)H3PO4·H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>different amount of H3BO3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>Co(OAc)2·4H2O·H3PO4·0.75H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(1) + (2)</td>
</tr>
<tr>
<td>S10</td>
<td>Co(OAc)2·4H2O·H3PO4·1H3BO3·[C4mpy]·[PF6]</td>
<td>200</td>
<td>7</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>different amount of H3BO3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

■ EXPERIMENTAL SECTION

Syntheses. Co2PO4OH is prepared under ionothermal conditions using the IL 1-buty-4-methylpyridinium hexafluorophosphate [C4mpy][PF6] as the solvent. A typical reaction, a mixture of cobalt(II) acetate tetrahydrate (Co(OAc)2·4H2O, 98%, ACROS), phosphoric acid (H3PO4, 85%, J. T. Baker), and [C4mpy]·[PF6] (99%, Merck) is reacted in a 3 mL Teflon-lined stainless steel autoclave at 200 °C for 7 d, followed by cooling to room temperature. The products were filtered off by suction, washed with deionized water and acetone, and dried at 60 °C for 1 d. Phase purity of the product was confirmed by the agreement between the experimental powder X-ray diffraction (PXRD) patterns and the simulated patterns based on the single-crystal structure analysis (Supporting Information, Figure S1).

Single-Crystal Structure Determination. A suitable single crystal of Co2PO4OH with dimensions of 0.12 × 0.02 × 0.02 mm was selected for single-crystal X-ray diffraction (SXRD) analysis. The data were collected at ambient temperature using graphite-monochromated Mo Kα radiation on an Image Plate Diffraction System, IPDS I (Stoe, Darmstadt, Germany). The data were corrected for Lorentz and polarization effects. Data correction was carried out with the program X-RED. A face-indexed numerical absorption correction (X-SHAPE) was applied. The structure was solved by direct methods and refined by full-matrix least-squares techniques with the SHELXTL crystallographic software package. The Co, P, and O atoms could be unambiguously located. See Supporting Information for experimental details on the crystal structure determination of Co2PO4OH and for further details of the crystal structure investigations.

Characterizations. PXRD data were collected on an image plate-GE670 Guinier camera (Huber, Rimming, Germany) with Mo Kα radiation λ = 0.71073 Å. FT-IR spectra were measured on a Bruker Alpha spectrometer with KBr pellets in the range of 4000–400 cm⁻¹. Ultraviolet–visible (UV–vis) absorption spectra were measured on an Agilent Cary 5000 spectrometer on a solid sample, using the internal diffuse reflection accessory. To avoid saturation, samples were ground with a 10-fold excess of BaSO4 prior to the measurements. The reflectance spectrum recorded of pure optical-grade BaSO4 was used as reference.

Magnetism. The magnetic susceptibility of Co2PO4OH was measured in a MPMS-XL7 apparatus (Quantum Design) on powder samples placed in a polycarbonate capsule and fixed with high purity inert wax to prevent the powder from moving under the influence of the applied high magnetic fields. Both the direct current (dc) and alternating current (ac) magnetic susceptibilities (χ) were measured. For determination of the dc magnetic susceptibility, a field of 0.1 T was used for the temperature-dependent measurement, and fields up to 7 T were used for the isothermal magnetizations at temperatures of 2, 5, 10, 20, and 30 K. The driving field in the ac measurements was 2 Oe, with frequencies ranging from 1 to 1000 Hz.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The original objective of our experiments was to produce complex cobalt hydroxyphosphates. Surprisingly, we obtained two different compounds, Co2PO4OH (1) and Co2PO4F (2), under quite similar synthesis conditions, using the IL 1-buty-4-methylpyridinium hexafluorophosphate [C4mpy][PF6] as the solvent and mineralizer. It was found that Co2PO4OH (1) crystallizes in the space group I4_1/amd, isotypic with the minerals camminate (Mg1.33[SO4(OH)0.66(H2O)0.33]) and lipscombite (Fe2+PO4(OH) (0 ≤ y ≤ 2/3). The competing phase, Co2PO4F (2), crystallizes isostructurally with triplite (Mn3PO4F) with the space group C2/c. To elucidate the mechanism of formation of Co2PO4X (X = OH, F), a systematic synthesis study was carried out. We explored the variation of various parameters such as stoichiometric ratios and concentrations of the starting materials. Table 1 summarizes the initial mixture compositions, crystallization conditions, and the phases obtained. By a careful choice of the reaction parameters we managed to obtain monophasic Co2PO4OH (1).

Pure Co2PO4OH (1) could be obtained by heating a molar composition of Co(OAc)2·4H2O (OAc = acetate), H3PO4, and 0.75 H3BO3 in [C4mpy][PF6] in a ratio of 1:1:0.75:1 at 200 °C for 7 d (sample S1). Upon halving the amount of the IL [C4mpy][PF6], a mixture of Co2PO4OH (1) and Co2PO4F (2) was obtained (sample S2). When further decreasing the amount of the IL, a new, unknown phase of poor crystallinity formed, and Co2PO4OH (1) could no longer be observed (sample S3). When doubling the amount of [C4mpy][PF6], Co2PO4OH (1) was obtained along with an amorphous pink powder (sample S4). When the amount of Co(OAc)2·4H2O was increased, biphasic mixtures of Co2PO4OH (1) and Co2PO4F (2) formed (sample S5), with (1) being dominant for increases of up to 1.5 times the original amount and (2) becoming the prevalent species thereafter (sample S6). Increases of up to double the amount of H3PO4 still led to pure Co2PO4OH (1) (sample S7), whereas decreases gave both Co2PO4OH (1) and Co2PO4F (2) in biphasic samples (sample S8). The initial pH of the starting mixtures was adjusted by fixed with high purity inert wax to prevent the powder from moving under the influence of the applied high magnetic fields. Both the direct current (dc) and alternating current (ac) magnetic susceptibilities (χ) were measured. For determination of the dc magnetic susceptibility, a field of 0.1 T was used for the temperature-dependent measurement, and fields up to 7 T were used for the isothermal magnetizations at temperatures of 2, 5, 10, 20, and 30 K. The driving field in the ac measurements was 2 Oe, with frequencies ranging from 1 to 1000 Hz.

The thermal stability of Co2PO4OH in air was determined using thermal gravimetric analysis, and the results are shown in
Supporting Information, Figure S2. Co₃PO₄OH remains stable under ambient conditions up to 400 °C, while Co₃PO₄F is stable up to 1000 °C.

Crystal Structure. Single-crystal structure analysis reveals that Co₃PO₄OH crystallizes in the tetragonal unit cell with space group I₄₁/amd (No. 141). The cell parameters are a = b = 5.2713(7) Å, c = 12.907(3) Å, V = 358.63(10) Å³, and Z = 4. For further structural details such as an atomic coordinate list and selected bond lengths and angles see Supporting Information. The structure of Co₃PO₄OH is characterized by a three-dimensional (3D) framework of \{CoO₆(OH)₂\} octahedra and monophosphate [PO₄] tetrahedra. The asymmetric unit of the crystal structure contains four crystallographically distinct atoms, one cobalt atom, one phosphorus atom, one oxygen atom, and one hydroxyl ion (Supporting Information, Figure S3). The cobalt atom is located on an inversion center (Wyckoff position 8 c) and has an octahedral coordination to four oxygen atoms located on a mirror plane (Wyckoff position 16 h) and two hydroxyl ions located on the cross point of an inversion axis \( \overline{4} \), a mirror plane, and a 2-fold axis (Wyckoff position 4 a). The Co(1)−O(1) and Co(1)−O(1H) bond lengths are 2.064(6) Å and 2.0832(3) Å, respectively. The cis O−Co−O bond angles range from 82.6(2)° to 97.4(2)°, whereas the trans angles are 180°. The phosphorus atom is located on the cross point of an inversion axis \( \overline{4} \), a mirror plane, and a 2-fold axis (Wyckoff position 4 b), and is involved in eight P−O−Co bonds via four tribridging oxygen atoms. The phosphate tetrahedra are quite regular, with P−O bond distances of 1.510(8) Å and with O−P−O angles varying from 108.7(7)° to 109.9(4)°.

FT-IR Spectroscopy. An FT-IR spectrum for Co₃PO₄OH recorded in the region of 4000–400 cm⁻¹ was collected to confirm the presence of Co−O−H moieties (Figure 2). The peak observed at 3527 cm⁻¹ can be attributed to the stretching vibration of the bridging −OH group of the octahedral CoO₆(OH)₂. Moreover, it is possible to observe another weak and broad band at around 3404 cm⁻¹, which is assigned to stretching vibrations of Co−O−H groups as was shown in [Co₂,Mn₃(III)(OH)PO₄] and Co₂(OH)(PO₄)₁₋ₓ(AsO₄)ₓ (0 ≤ x ≤ 1). The two broad absorption bands in the neighborhood of 2891 and 2512 cm⁻¹ are frequently interpreted as a doublet produced by the O(1H)−H···O(1) stretching vibration split by proton tunneling between two equilibrium positions along the O−O axis (\( d_{O(1H)−O(1)} = 2.7379(89) \) Å).

The peak at 889 cm⁻¹ is assigned to the bridging −OH in the Co−OH−Co bending vibration as was shown in NaCo₃(III)(OH)(PO₄)₂(1/4)H₂O. These large absorption bands together with the weak peak at 1632 cm⁻¹ indicate the presence of OH groups in the Co₃PO₄OH (1) structure. The bands at around 1114 cm⁻¹ and 1025 cm⁻¹ are attributed to the asymmetric stretching vibration of the phosphate tetrahedra. The bands below 600 cm⁻¹ are attributed to the deformation vibrations of O−P−O and can be probably
coupled to the corresponding asymmetric stretching modes of the cobalt oxygen bonds.25a

UV–visible Absorption Spectroscopy. The UV–vis absorption spectrum of Co$_2$PO$_4$OH (1) was recorded on a powder sample diluted by a 10-fold excess of BaSO$_4$ (Figure 3).

As expected for $d^7$ Co$^{3+}$ in an octahedral-like coordination, three major transition bands are visible: the first one at 6860 cm$^{-1}$, which is split into two lines, the second one at 14 390 cm$^{-1}$, and the third one at 18 550 cm$^{-1}$ with a weak shoulder at 20 900 cm$^{-1}$. This splitting can be explained by a Jahn–Teller distortion: reducing the symmetry from full orbital contribution ($L^2 + S^2$) = $3/2$ (d$^7$, Co$^{3+}$) a magnetic moment of 4.71 $\mu_B$ is obtained, and for a Co$^{3+}$ with full orbital contribution ($L + S = 1$), the value can reach 5.2 $\mu_B$. Hence, Co$^{3+}$ in Co$_2$PO$_4$OH has a significant orbital contribution ($L$) to the magnetic moment, but $L$ is not fully evolved. The extracted Curie–Weiss constant ($\Theta_{CW} = -49.7$ K) is negative, pointing to predominant antiferromagnetic interactions in the spin ground state. All of these observations agree with what has been measured for orthorhombic Co$_2$PO$_4$OH,30 but the tetragonal modification exhibits other magnetic features at lower temperatures. As judged from both dc (Figure 4) and ac magnetic susceptibility data (upper inset Figure 4), the first magnetic anomaly starts to set in around 20 K. The upper-left curves represent the suggested magnetization anisotropy at 2 K, as discussed in the text for a theoretical single crystal. Both lower-right insets are structural motifs of tetragonal Co$_2$(PO$_4$)(OH) with a suggested magnetic structure with black arrows and crystal. Both lower-right insets are structural motifs of tetragonal Co$_2$(PO$_4$)(OH) as function of temperature, displaying both field-cooled and zero-field-cooled data. The lower inset is a magnification of $\chi'$ at high temperatures including a Curie–Weiss fit (dashed line) together with the values obtained from that fit. Both real ($\chi'$) and imaginary ($\chi''$) parts of $\chi$ are shown in the upper inset, where field driving frequency was increased from 1 to 1000 Hz, as indicated with a thin arrow close to the maximum in $\chi'$.

Figure 4. Magnetic susceptibility ($\chi$) of tetragonal Co$_2$(PO$_4$)(OH) as function of temperature, displaying both field-cooled and zero-field-cooled data. The lower inset is a magnification of $\chi'$ at high temperatures including a Curie–Weiss fit (dashed line) together with the values obtained from that fit. Both real ($\chi'$) and imaginary ($\chi''$) parts of $\chi$ are shown in the upper inset, where field driving frequency was increased from 1 to 1000 Hz, as indicated with a thin arrow close to the maximum in $\chi'$.

Figure 5. Magnetization as function of magnetic field (B) at several different temperatures, as indicated close to the corresponding curve. The upper-left curves represent the suggested magnetization anisotropy at 2 K, as discussed in the text for a theoretical single crystal. Both lower-right insets are structural motifs of tetragonal Co$_2$(PO$_4$)(OH) with a suggested magnetic structure with black arrows and the magnetically induced states with B along c (gray arrows) and B (purple arrow).

Figure 5. Magnetization as function of magnetic field (B) at several different temperatures, as indicated close to the corresponding curve. The upper-left curves represent the suggested magnetization anisotropy at 2 K, as discussed in the text for a theoretical single crystal. Both lower-right insets are structural motifs of tetragonal Co$_2$(PO$_4$)(OH) with a suggested magnetic structure with black arrows and the magnetically induced states with B along c (gray arrows) and B (purple arrow).
field does not change on going from 20 to 2 K. The absolute magnitude of the polarization is decisive for the spin ground state: a value of 0.75 μ_B (Figure 5) of theoretically 3 μ_B points to a ferri- or canted antiferro-magnetic ground state, which agrees with the fact that a negative θ_{CW} and a T_C (not a T_N) are observed. In tetragonal Co₂PO₄OH, for Co²⁺ there is only one crystallographically independent site (Wyckhoff symbol 8c). Thus, assuming that no temperature-dependent structural transition is involved, the occurrence of a ferrimagnetic state is not likely as in that case an uneven contribution of magnetic moment of at least two crystallographically independent Co²⁺ sites is necessary. Thus, with only one crystallographic site present a canted antiferromagnetic spin order as the ground state is more likely.

The crystal structure of Co₂PO₄OH features columns of tilted [CoO₄(OH)₂] octahedra face-shared by three oxygen atoms, running along the a (≠ b) axes (Figure 5). From the structure, two magnetic coupling paths can be identified: (i) the coupling along the columns and (ii) the coupling between the columns. The observed competing magnetic interactions thus can be explained if (i) is of a ferromagnetic and (ii) is of an antiferromagnetic nature (or vice versa). The magnetic structure of orthorhombic Co₂PO₄OH contains ferromagnetic columns, as determined by neutron scattering. Thus, all columns in the tetragonal modification are assumed to contain parallel coupled spins, and the 4₁ screw axis is conforming to a continuously rotating spin direction from one column to the next along the unique axis (inset, Figure 5).

Without further data, it is difficult to interpret the two steps in the 2 K magnetization data (Figure 5), especially from an isotropic powder. However, a complex spin-flip transition along a single crystallographic easy axis appears unlikely. Hence, it is fair to assume that the complex transition involves two components: one along the unique crystallographic axis (c) and a second perpendicular to it. Note that any in-plane ferromagnetic component has to break the tetragonal symmetry, and such a transition should be of first order, that is, hysteretic. Therefore it is possible to postulate that the hysteretic part of the transition belongs to a spin-flip in-plane (Lc) component, and the nonhysteretic part is related to a spin-flip component oriented along the unique axis (lc), shown in the lower-right inset in Figure 5. The size of the magnetization parts naturally corresponds to the relative amount of spins that are flipped or flopped, but more data are necessary to confirm these assumptions. However, by flipping one spin out of four within the ab plane, the magnetization changes by 0.75 μ_B (3 μ_B/4), which agrees quite well with the observations, considering that the measured sample is a powder with all crystallographic directions statistically equally represented. Neutron diffraction data would be necessary to fully understand the spin structure in tetragonal Co₂(PO₄)OH, and these investigations are planned in the near future.

CONCLUSIONS

A new framework cobalt phosphate, Co₂PO₄OH, has been successfully prepared under ionothermal conditions, using the IL 1-butyl-1-methylpyridinium hexafluorophosphate, [C₅pympy][PF₆], as the solvent and mineralizer. To allow for the determination of optical and magnetic behavior, phase-pure materials were obtained, and the optimal synthesis conditions were found by varying the stoichiometry of the reagents. Co₂PO₄OH crystallizes in the tetragonal space group I4₁/amd. It is built up by face-sharing Co octahedra chains parallel to the a and b axes, which are arranged in a simple cubic rod packing. The rods are linked through tribridging O(2)H atoms linking the Co octahedra to six-membered rings. Finally, PO₄ tetrahedra interconnect four chains of CoO₄(OH)₂ octahedra. Further analytical methods such as FT-IR and UV–vis spectroscopy corroborate the crystal structure found. Co₂PO₄OH stays thermally stable up to 400 °C in air. Magnetic susceptibility measurements show paramagnetic behavior near room temperature but an anomaly at about 20 K, which may be the compound’s Curie temperature (T_C). A ferromagnetic moment arises below this temperature. Following the Curie–Weiss fit, considerations of crystallographic site occupancies of Co²⁺, two magnetic coupling paths can be identified: one ferromagnetic along the columns and another antiferromagnetic between the columns. The spin ground state is probably canted antiferromagnetic. The magnetization curve observed at 2 K consists of a combination of a spin-flip and a spin-flip transition. Neutron diffraction measurements are necessary to unveil the magnetic structure-related details unambiguously.


(18) X-Red 1.22, Stoe Data Reduction Program (C); Stoe & Cie GmbH: Darmstadt, Germany, 2001.

(19) X-Shape 1.06, Crystal Optimization for Numerical Absorption Correction (C); Stoe & Cie GmbH: Darmstadt, Germany, 1999.


