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Synthesis, crystal structure and optical properties of the *catena*-metaphosphates Ce(PO₃)₄ and U(PO₃)₄

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In memory of Friedrich Liebau

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Cerium / Uranium / Polyphosphate / Crystal structure / Absorption spectrum

Abstract. The *catena*-metaphosphates of tetravalent cerium and tetravalent uranium were obtained as phase pure crystalline powders by reaction of the respective dioxides with phosphoric acid at 500 °C. Ce(PO₃)₄ and U(PO₃)₄ crystallise in space group *C2/c* ($Z = 16$, $a_{\text{Ce}} = 13.7696(3) \text{ \AA}$, $b_{\text{Ce}} = 29.7120(7) \text{ \AA}$, $c_{\text{Ce}} = 8.9269(2) \text{ \AA}$, $\beta_{\text{Ce}} = 90.00(1) \text{ \AA}^3$ and $a_{\text{U}} = 13.786(3) \text{ \AA}$, $b_{\text{U}} = 29.843(6) \text{ \AA}$, $c_{\text{U}} = 8.9720(18) \text{ \AA}$, $\beta_{\text{U}} = 90.01(3) \text{ \AA}^3$). The vibrational and optical spectra of pale yellow Ce(PO₃)₄ and emerald-greenish U(PO₃)₄ are also reported.

Introduction

Catena-metaphosphates contain polymeric chains of corner-sharing PO₄ tetrahedra. Depending on size and charge of the respective counterion these chains are folded or curled differently. In the meantime we solved the crystal structures of *catena*-metaphosphates of divalent ions like α -Sr(PO₃)₂ [1] or CaBa(PO₃)₄ [2] and of trivalent ions like α -Ln(PO₃)₃ and β -Ln(PO₃)₃ ($Ln = \text{Sc, Y, Gd} \dots \text{Lu}$) [3–5]. From a chemical point of view it is very interesting how rigid *catena*-metaphosphate chains manage to fold around rather tiny tetravalent ions like Ce⁴⁺ and U⁴⁺.

From a materials scientist's view compounds of tetravalent cerium are known as efficient UV absorber materials and are used as additives in respective glasses [6], e.g. windows in space vehicles [7]. For such applications the absorption spectrum is relevant which was not reported so far. Insoluble compounds of tetravalent uranium may be interesting for the final deposition of radioactive uranium waste. Uranium ions strongly bound in a *catena*-metaphosphate matrix should be hard to dissolve as already observed for *catena*-metaphosphates of divalent and trivalent ions [1–5].

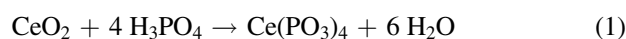
In this contribution we investigated the crystal structures of the systematically twinned title compounds and

solved chemical inconsistencies of previous investigations [8, 9] like strongly distorted phosphate tetrahedra. We also investigated the vibrational spectra and the optical reflection spectra of the title compounds.

Experimental Section

Synthesis of Ce(PO₃)₄

The synthesis of Ce(PO₃)₄ started according to Eq. (1) from cerium dioxide (250 mg, 1.45 mmol, phase pure) which was suspended in 5 ml conc. phosphoric acid as flux and heated in a platinum crucible to 500 °C with a heating rate of 180 °C/h. The mixture was maintained at this temperature for six hours before it was cooled to room temperature by switching off the furnace. After washing off the flux with hot water cerium(iv) *catena*-metaphosphate was obtained as pale yellow needles.



Synthesis of U(PO₃)₄

U(PO₃)₄ was synthesised in a two-step process starting with an oxidation of uranyl acetate UO₂(CH₃COO)₂ · 2 H₂O (423 mg, 1.00 mmol, phase pure) in air (300 °C, 12 h) to brown uranium dioxide. 250 mg of this UO₂ were subsequently reacted with phosphoric acid, analogously to the procedure given for the cerium compound. Finally uranium(iv) *catena*-metaphosphate was obtained as emerald-green needles, which could not be dissolved in water or diluted acids and bases.

X-ray Powder Diffraction

The crystalline samples were enclosed in glass capillaries with 0.2 mm diameter and investigated at room temperature in Debye–Scherrer geometry on a STOE Stadi P powder diffractometer with Ge(111)-monochromatized MoK_α radiation (linear PSD detector, step width 0.5°, acquisition time: 90 s/step). The obtained crystalline pro-

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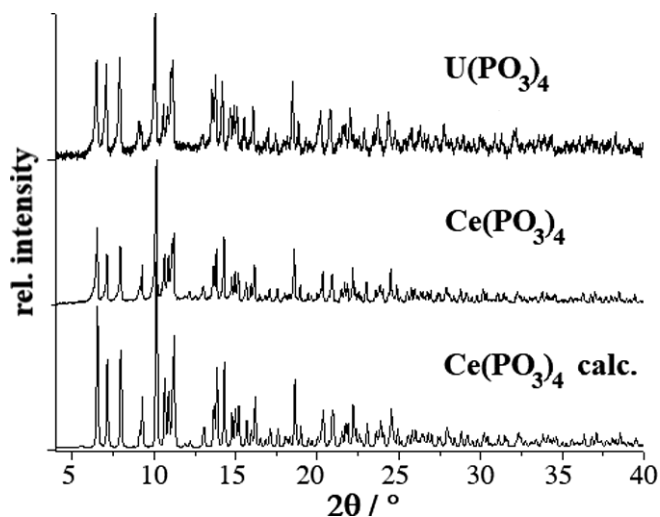


Fig. 1. Comparison of measured diffraction patterns of $\text{U}(\text{PO}_3)_4$ (top) and $\text{Ce}(\text{PO}_3)_4$ to a calculated powder diffraction pattern on the basis of our structure model of $\text{Ce}(\text{PO}_3)_4$ (bottom).

ducts $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$ were found to be phase pure (Fig. 1).

Crystal Structure Determination

Single-crystal X-ray diffraction data were collected on a Bruker AXS CCD diffractometer fitted with an APEX-II detector using MoK_α radiation at room temperature and corrected for absorption by applying a multi-scan correction [10]. The crystal structures of $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$ were solved by direct methods using the SHELXTL program package [11] in space group $C2/c$ (no. 15) and refined with anisotropic displacement parameters for all metal and phosphorus atoms. The crystal structure solution and the subsequent refinement of the structure model was performed also in the smaller subcells – ignoring the superstructure reflections – but significantly worse reliability factors and, more important, the occurrence of many disordered structure fragments as well as extremely large thermal displacement parameters even for the heavy atoms confirmed the finally accepted supercell as the correct one. Moreover, we tried to find a chemically feasible structure model in the higher symmetric orthorhombic crystal system. All attempts yielded structure models with unreasonably short atom distances and a manifold of “disordered” oxygen positions which could be dissolved only by choosing space group $C2/c$. Also, in the final unit cell a pseudomerohedral twinning with the matrix $(-1\ 0\ 0/0\ -1\ 0/0\ 0\ 1)$ had to be considered with refined fractions of approx. 50% for each domain. All refinements were also performed in space group Cc (no. 9) but all gave less stable refinements with significantly worse reliability factors. The phase identification was carried out by powder X-ray diffraction. Relevant crystallographic data and further details of the X-ray data collection are summarised in Table 1. Table 2 lists selected interatomic distances and angles in $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$. Further details of the crystal structure investigation presented in this work may be obtained from the Fachinformationszentrum Karlsruhe, D-76344

Table 1. Crystallographic data of $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$ (estimated standard deviations in parentheses)

	$\text{Ce}(\text{PO}_3)_4$	$\text{U}(\text{PO}_3)_4$
temp./K	298(2)	298(2)
$M/g\ mol^{-1}$	456.00	553.91
colour	pale yellow	emerald green
crystal dim./mm	$0.01 \times 0.04 \times 0.05$	$0.01 \times 0.03 \times 0.04$
space group	$C2/c$ (no. 15)	
$a/\text{Å}$	13.7696(3)	13.786(3)
$b/\text{Å}$	29.7120(7)	29.843(6)
$c/\text{Å}$	8.9269(2)	8.972(2)
$\beta/^\circ$	90.00(1)	90.01(3)
cell vol./ Å^3	3652.19(14)	3691.3(13)
Z	16	
$\rho_{\text{X-ray}}/g\ cm^{-3}$	3.317	3.987
μ/mm^{-1}	5.75	18.35
$F(000)$	3424	3968
radiation	MoK_α	
diffractometer	Bruker AXS CCD (APEX-II)	STOE IPDS 2
abs. corr.	multi-scan	numerical
index range	$\pm 17/\pm 38/\pm 11$	$\pm 17/\pm 38/\pm 11$
$2\theta_{\text{max}}/^\circ$	55.0	55.0
refl. collected	34567	9892
independent refl.	4189	4257
$I/\sigma > 4$	1927	1748
avg. intens. I/σ (subcell)	12.0	12.9
R_{int}/R_σ	0.136/0.069	0.0471/0.0732
R_1	0.058	0.044
wR_2	0.078	0.082
GooF	1.104	0.912
res. electron dens.	1.32/–1.16	1.37/–1.82

Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-423884 ($\text{Ce}(\text{PO}_3)_4$) and CSD-423883 ($\text{U}(\text{PO}_3)_4$), the names of the authors, and citation of this publication.

Table 2. Selected interatomic distances/pm and angles/ $^\circ$ in $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$; estimated standard deviations in parentheses.

	$\text{Ce}(\text{PO}_3)_4$	$\text{U}(\text{PO}_3)_4$
$\text{Ce}-\text{O}^{\text{term}}$	223.5(3)–242.2(6)	
$\text{U}-\text{O}^{\text{term}}$		224.7(3)–242.1(9)
$\text{P}-\text{O}^{\text{term}}$	144.3(7)–151.5(6)	145.5(9)–151.7(9)
$\text{P}-\text{O}^{\text{br}}$	155.1(6)–162.6(6)	156.5(7)–162.3(9)
$\text{O}^{\text{term}}-\text{P}-\text{O}^{\text{br}}$	105.0(3)–114.3(3)	105.7(4)–115.4(3)
$\text{O}^{\text{term}}-\text{P}-\text{O}^{\text{term}}$	110.0(2)–121.7(2)	110.2(3)–122.8(2)
$\text{O}^{\text{br}}-\text{P}-\text{O}^{\text{br}}$	95.9(4)–103.2(2)	96.1(5)–102.2(5)
$\text{P}-\text{O}^{\text{br}}-\text{P}$	128.0(4)–145.6(3)	125.7(6)–148.4(3)

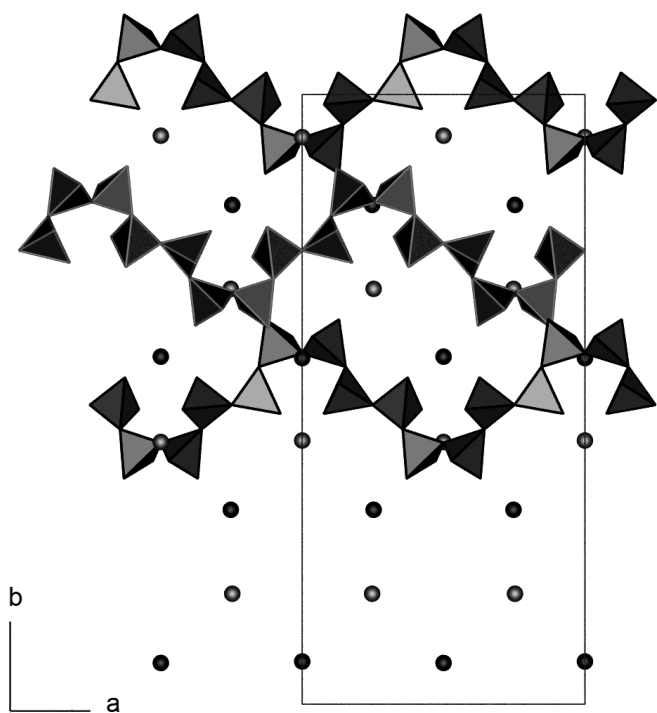


Fig. 2. Crystal structure of $\text{Ce}(\text{PO}_3)_4$; the phosphate tetrahedra are drawn as closed polyhedra, the cerium atoms are represented by grey and black spheres representing layers A and B of the h.c.p., respectively.

Crystal Structure of $M(\text{PO}_3)_4$ ($M = \text{Ce}, \text{U}$)

Overview

The crystal structures of the *catena*-metaphosphates of tetravalent cerium and uranium are isotypic. In both, the metal atoms are arranged in a hexagonal closest packing with the A and B layers being perpendicular to the c axis of the pseudo-orthorhombic unit cell. This structural feature is not really surprising due to the presence of particles with an extraordinarily large charge density forcing the Ce^{4+} ions into a highly symmetric arrangement. In between this packing the phosphate chains run along the $[101]$ direction as shown in Fig. 2. This representation also provides a view of the phosphate chains folding around the cations to realise almost regular eightfold coordination environments best described as square-antiprismatic as presented in Fig. 3. Accordingly, each cation site is coordinated by terminal oxygen atoms belonging to five different metaphosphate chains.

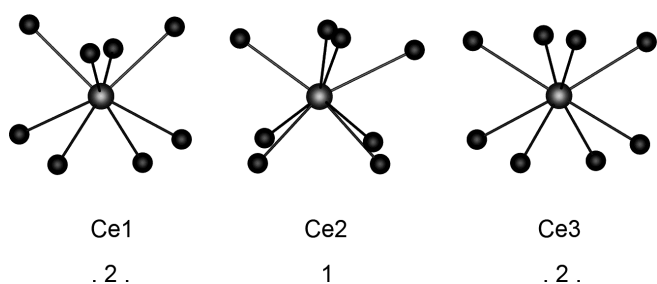


Fig. 3. Coordination polyhedra of Ce^{4+} in $\text{Ce}(\text{PO}_3)_4$ viewed perpendicularly to (010) , the site symmetries are given.

Bond distances and angles

As normally observed [1–5], within phosphate chains the bonds from phosphorus atoms to the bridging oxygen atoms are significantly longer compared with those to the terminal oxygen atoms, and this also holds for $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$: in cerium *catena*-metaphosphate the bondlengths $\text{P}-\text{O}^{\text{term}}$ range from 144.3(7) to 151.5(6) pm (uranium *catena*-metaphosphate: 145.5(9)–151.7(9) pm), and the bondlengths $\text{P}-\text{O}^{\text{br}}$ range from 155.1(6) to 162.6(6) pm (156.5(7)–162.3(9) pm).

A similar behaviour is found for the $\text{O}-\text{P}-\text{O}$ angles with the larger ones being the $\text{O}^{\text{term}}-\text{P}-\text{O}^{\text{term}}$ angles and $\text{O}^{\text{br}}-\text{P}-\text{O}^{\text{br}}$ angles the smaller. Accordingly, the $\text{O}^{\text{term}}-\text{P}-\text{O}^{\text{term}}$ angles in $\text{U}(\text{PO}_3)_4$ amount in average 117.9° (cerium *catena*-metaphosphate: 117.8°), the $\text{O}^{\text{br}}-\text{P}-\text{O}^{\text{br}}$ angles 99.2° (98.9°), while the $\text{O}^{\text{term}}-\text{P}-\text{O}^{\text{br}}$ angles are in average 109.5° (109.6°), the ideal tetrahedral angle.

The heavy atoms are coordinated by eight terminal oxygen atoms of the polymeric phosphate chains. In the case of $\text{Ce}(\text{PO}_3)_4$ coordination distances between 223.5(3) and 242.2(6) pm were found, in $\text{U}(\text{PO}_3)_4$ the $\text{U}-\text{O}$ distances range from 224.7(3) to 242.1(9) pm. Both distance ranges agree very well with the sum of the ionic radii, *i.e.* 232 pm for $\text{Ce}^{4+}-\text{O}^{2-}$ and 235 pm for $\text{U}^{4+}-\text{O}^{2-}$ [12].

Discussion

Previously published structure models on the two title compounds (Ref. [8, 9]) – refined in the orthorhombic space group $Pb\bar{c}n$ – suffered from strongly distorted phosphate tetrahedra; for *catena*-phosphates minor deviations from the ideal tetrahedral symmetry are expected due to an enhanced bond-order for the bonds to terminal oxygen atoms compared with the bonds to bridging oxygen atoms; this fact also holds for all silicates containing Q1, Q2 or Q3 tetrahedra [13]. Those strong deviations indicated twice, the doubling of the unit cell as well as the twinning resolved in our contribution in a pseudo-orthorhombic monoclinic setting. An excellent measure for deviations of phosphate tetrahedra from the ideal symmetry is the method suggested by *Balic-Žunic* and *Makovicky* [14, 15] which we already applied to the poly- and cyclophosphates $\beta\text{-Ln}(\text{PO}_3)_3$ [4] and $\text{Ba}_2(\text{P}_4\text{O}_{12}) \cdot 3.5 \text{H}_2\text{O}$ [16]. For these we identified typical values for condensed phosphate tetrahedra below 1%. All tetrahedra in our structure models of $M(\text{PO}_3)_4$ ($M = \text{Ce}, \text{U}$) show distortions well within this range.

Classification of the chains according to *Liebau*

According to *Liebau*'s nomenclature for silicates [13] the chains are classified as unbranched achter single chains. Such chains are rarely found in silicate chemistry. A recent example is $\text{Rb}_2\text{LnGa}(\text{Si}_4\text{O}_{12})$ ($\text{Ln} = \text{Y}, \text{Eu}, \text{Gd}, \text{Tb}$) [17] in which the silicate chains adopt a different repetition unit.

To our best knowledge, the achter single chains of the *catena*-metaphosphates in our contribution represent a novel chain arrangement unknown so far in silicate and phosphate chemistry.

Table 3. Results of the MAPLE calculation for $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$ compared with the MAPLE calculations on previously known compounds.

$\text{Ce}(\text{PO}_3)_4$	$\text{U}(\text{PO}_3)_4$
MAPLE = 100756 kJ/mol	MAPLE = 100272 kJ/mol
MAPLE (CeP_2O_7 [21] + P_2O_5 [22]) = 100764 kJ/mol	MAPLE (UP_2O_7 [23] + P_2O_5 [22]) = 99441 kJ/mol
$\Delta < 0.01\%$	$\Delta = 0.8\%$

Electrostatic Calculations

We checked our structure models for electrostatic reasonability using calculations based on the MAPLE concept (MAPLE = Madelung Part of Lattice Energy) [18–20]. A structure model is electrostatically consistent if the sum of MAPLE values of chemically similar compounds deviates from the MAPLE value of the compound of interest below 1%. According to our calculations the structure models of $\text{Ce}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$ thus show electrostatic consistency (Table 3).

Optical Spectroscopy

$\text{Ce}(\text{PO}_3)_4$

The diffuse reflection spectrum of $\text{Ce}(\text{PO}_3)_4$ is shown in Fig. 4. We observed the characteristic $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ charge-transfer transition with an onset at 420 nm (2.9 eV). This is a slightly lower transition energy compared with other compounds containing tetravalent cerium like Sr_2CeO_4 (3.2 eV), SrCeO_3 (3.5 eV) and CeO_2 (3.2 eV) [24].

The measured UV-Vis absorption spectrum is in agreement with the pale yellow colour of the title compound.

$\text{U}(\text{PO}_3)_4$

The diffuse reflection spectrum of $\text{U}(\text{PO}_3)_4$ is shown in Fig. 5. The characteristic absorptions of the uranium ions were found in the region between 400 and 700 nm, which

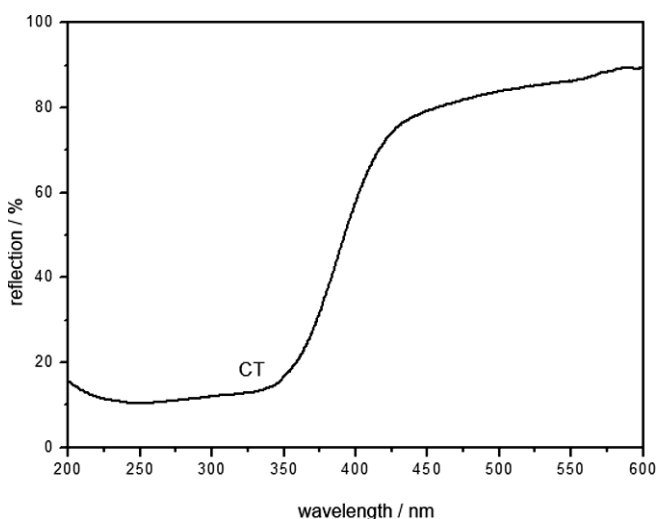


Fig. 4. UV-Vis reflection spectrum of $\text{Ce}(\text{PO}_3)_4$; the charge-transfer transition is indicated.

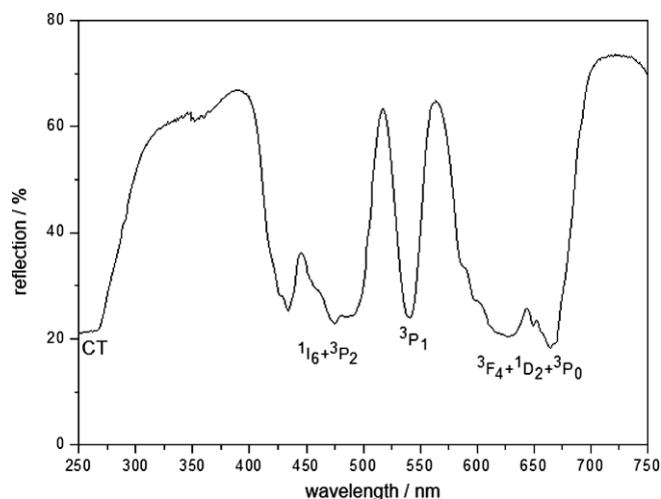


Fig. 5. UV-Vis reflection spectrum of $\text{U}(\text{PO}_3)_4$.

are due to the $5f-5f$ transitions of U^{4+} ($[\text{Rn}] 5f^2$; ground state $^3\text{H}_4$). In contrast to the $4f$ states the $5f$ states are subject to a significant crystal field splitting. Therefore the spectral position of the absorptions depends strongly from the coordination environment. The surrounding of the uranium ions in $\text{U}(\text{PO}_3)_4$ was found to be similar to that in UF_4 [25]. All relevant $5f-5f$ transitions in Fig. 5 are indicated according to the well known energy level scheme of U^{4+} with respect to the ground state $^3\text{H}_4$ [26]. The measured UV-Vis absorption spectrum is in agreement with the emerald greenish colour of uranium *catena*-metaphosphate.

Vibrational Spectroscopy on $\text{Ce}(\text{PO}_3)_4$

Fig. 6 shows the infrared and Raman spectra of cerium *catena*-metaphosphate. The infrared spectra of *catena*-metaphosphates are not significantly different from those of *catena*-oligophosphates [27]. The only characteristic bands should be found in the region between 800 and 650 cm^{-1} , where the number of bands should correspond to the periodicity of the phosphate chain. Normally, this holds quite reliably only for low chain periodicities. In the infrared spectrum of $\text{Ce}(\text{PO}_3)_4$ four broad bands are detected in

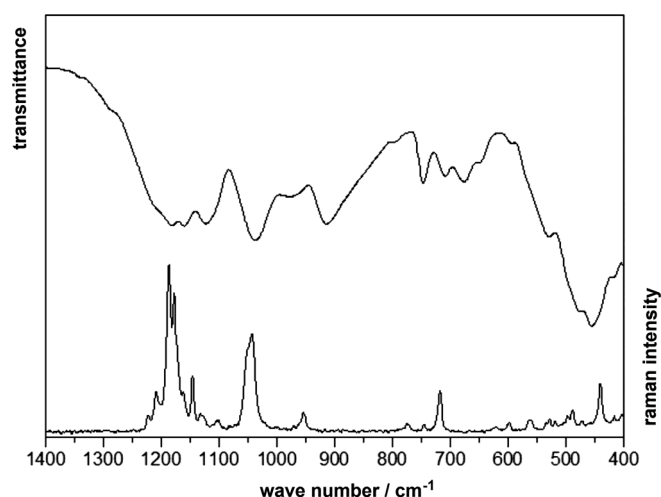


Fig. 6. Infrared and Raman spectra of $\text{Ce}(\text{PO}_3)_4$.

this region. This is not surprising since both wings of the achter single chain repeating unit are rather similar. The characteristic frequencies of *catena*-metaphosphates such as the $\nu_{\text{as}}(\text{PO}_2)$ are detected between 1100 and 1300 cm⁻¹, the rather intense $\nu_{\text{as}}(\text{POP})$ at 913 cm⁻¹ and $\nu(\text{PO}^{\text{term}})$ ranging from 1010 up to 1080 cm⁻¹. Additionally, the Raman spectra of Ce(PO₃)₄ show strong vibrations in the region between 1020 and 1200 cm⁻¹ ($\nu_{\text{s}}(\text{PO}^{\text{term}})$), and at 719 cm⁻¹ ($\nu_{\text{s}}(\text{POP})$). Thus the observed vibrational data are in good agreement with the expected values.

Conclusion

In this contribution we shed light on the crystal structures of the *catena*-metaphosphates of tetravalent cerium and uranium. Our structure refinements eliminate structural inconsistencies found in the first crystal structure reports of both compounds [8, 9]. We also presented the optical reflection spectra for the first time. The optical absorptions reveal basically the expected behaviour as well as the vibrational spectra which are in accordance with our structure model. Moreover, cerium *catena*-metaphosphate proved to be an efficient absorber material for the whole UV range.

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