

Supplementary Information

Sodium hypodiphosphate – new ionic conductor. Synthesis, stability, conductivity and 3D electron diffraction crystal structure

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Syntheses and crystallizations

All reagents, i.e. red phosphorus ($\geq 97.0\%$, Sigma-Aldrich), HCl (35-38%, Chempur), NaOH (p.a., Stanlab), H_2O_2 (p.a., 30%, Stanlab), ethanol (p.a., 96%, POCh S.A.), were used as obtained commercially without further purification. Dowex 50- H^+ ion exchange resin, 2–100 mesh (Serva), was regenerated after use by washing it with 3 M HCl and then with water until the pH was neutral.

Synthesis of $\text{Na}_2(\text{H}_2\text{P}_2\text{O}_6)\cdot 6\text{H}_2\text{O}$

This starting material was prepared by the method published by Yoza & Ohashi, i.e. by the reaction of red phosphorus with a dilute solution of hydrogen peroxide (H_2O_2) at room temperature, and subsequent addition of NaOH solution until pH was 4.6.^{S1} The identity of the compound^{S2} was confirmed by PXRD (Fig. S1).

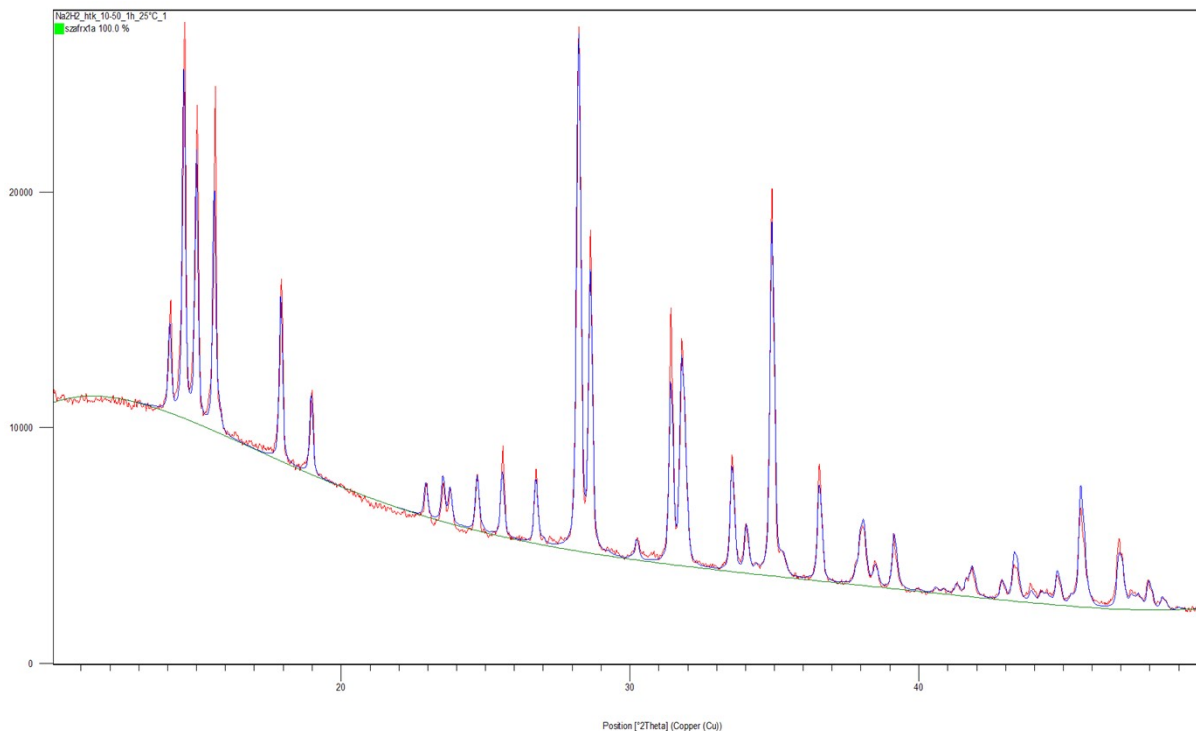


Figure S1. Experimental PXRD pattern for $\alpha\text{-Na}_2(\text{H}_2\text{P}_2\text{O}_6)\cdot 6\text{H}_2\text{O}$ (red line) and Rietveld-fitted theoretical pattern (blue line) generated from single crystal data.

Synthesis of $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$

$\text{Na}_2(\text{H}_2\text{P}_2\text{O}_6)\cdot 6\text{H}_2\text{O}$ (314.0 mg, 1.0 mmol) was mixed with 0.1 M NaOH (20 ml, 2.0 mmol). The solution was heated at 80 °C to reduce its volume to about 10 ml. Then 25 ml of ethanol was added to precipitate the product (colourless blocks), which was separated and washed with ethanol. The identity of the compound was confirmed by PXRD (Fig. S2).

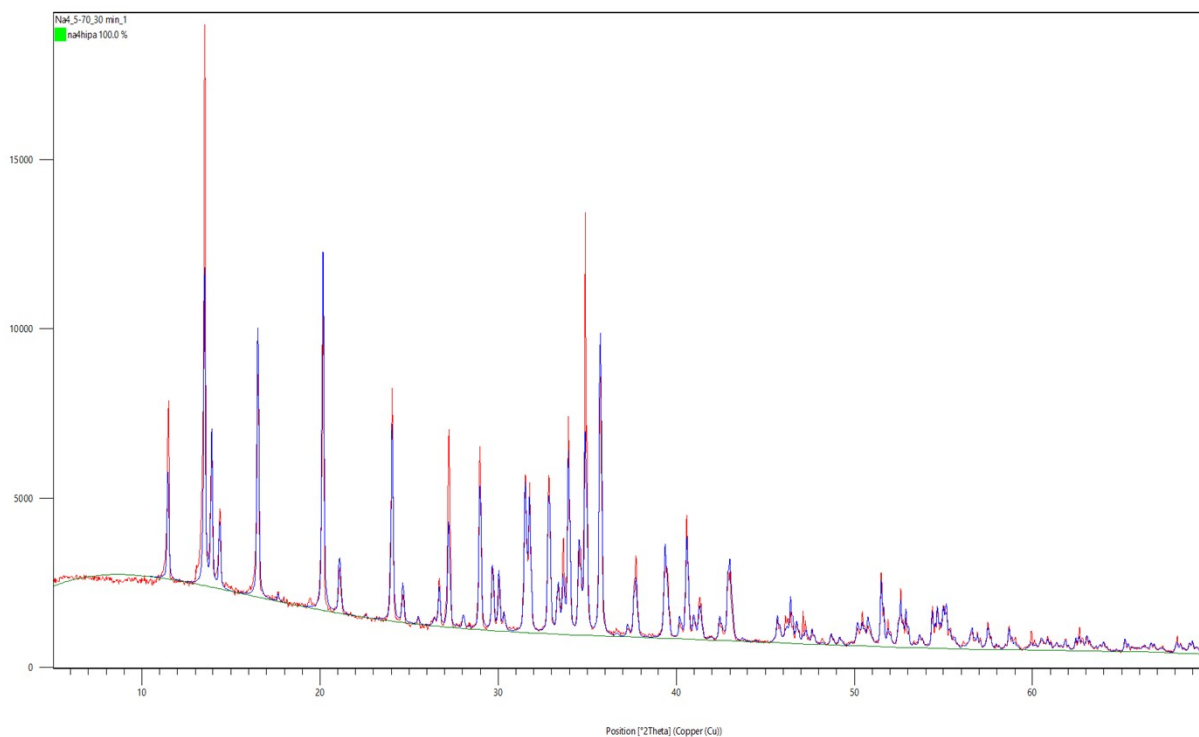


Figure S2. Experimental PXRD pattern for $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ (red line) and Rietveld-fitted theoretical pattern (blue line) generated from single crystal data.

Synthesis of $\text{Na}_4(\text{P}_2\text{O}_6)$

A polycrystalline sample of $\text{Na}_4(\text{P}_2\text{O}_6)$ was obtained by dehydration of its decahydrate, $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$, by annealing it at 100 °C. We were unable to obtain monocrystals of $\text{Na}_4(\text{P}_2\text{O}_6)$ big enough for the single crystal X-ray diffraction studies. The crystal structure was determined by 3D-ED and refined with the use of PXRD (Fig. S3).

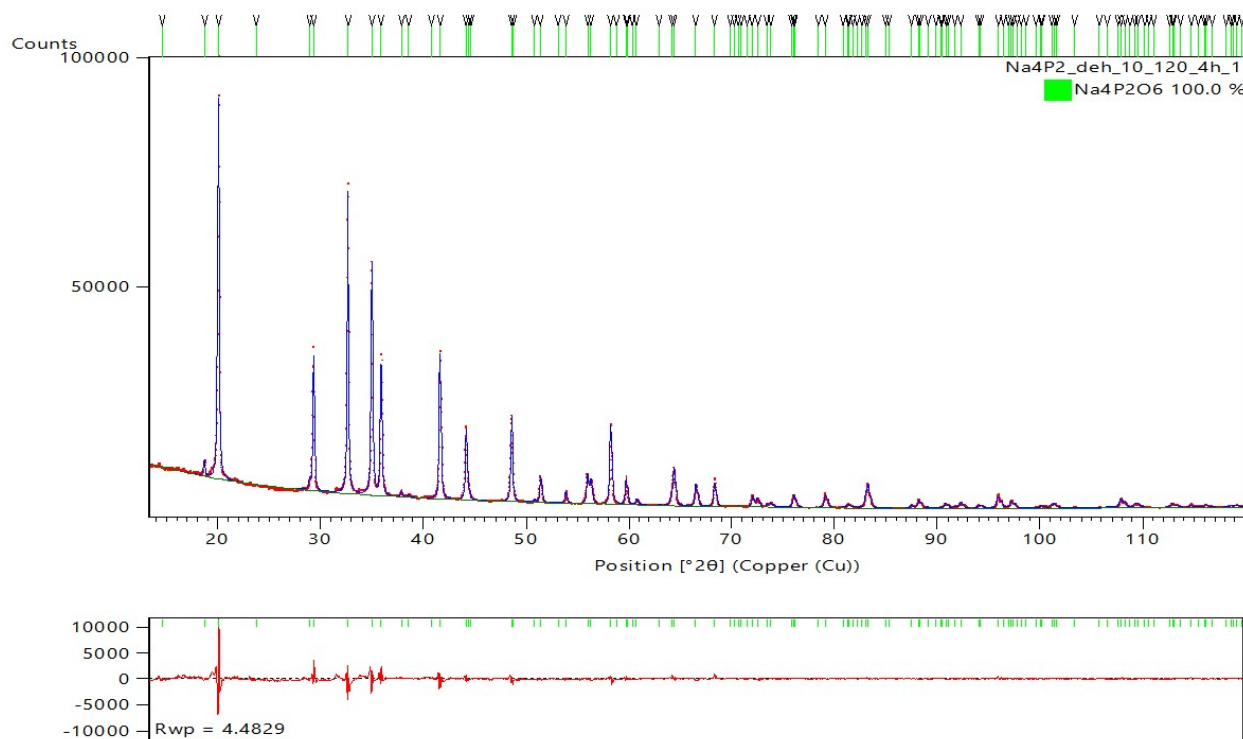


Figure S3. Experimental PXRD pattern for $\text{Na}_4(\text{P}_2\text{O}_6)$ (red dots) and Rietveld-fitted theoretical pattern (blue line) generated from 3D-ED single crystal data.

Single crystal X-ray diffraction (SC-XRD) for Na₄(P₂O₆)·10H₂O

SC-XRD data for Na₄(P₂O₆)·10H₂O were collected at 100 K on an Oxford Diffraction Xcalibur PX κ-geometry diffractometer using Mo Kα radiation (for details see Table S1). Data collections, cell refinements, data reductions and analyses were carried out with *CrysAlis CCD* and *CrysAlis RED*.⁵³ Data were corrected for Lorentz, polarization, and absorption effects.

The refinement of the crystal structure of Na₄(P₂O₆)·10H₂O was started by using the coordinates of non-H atoms taken from the 223 K structure published before (ICSD 424365).⁵⁴ Then all of the atoms were shifted by the vector (0, -0.5, 0) to place them in the unit cell. The structure was refined in Olex2⁵⁵ on *F*² by a full-matrix least-squares method using the *SHELXL* program⁵⁶ with anisotropic thermal parameters for the non-H atoms. Hydrogen atoms were found in difference Fourier maps and were refined freely.

Table S1. X-ray diffraction experimental details for the crystal of Na₄(P₂O₆)·10H₂O

CSD Deposition Number	2246556
Chemical formula	H ₂₀ Na ₄ O ₁₆ P ₂
<i>M_r</i> (g mol ⁻¹)	430.06
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.946(2), 6.9461(10), 14.360(2)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	90, 115.11(2), 90
<i>V</i> (Å ³)	1530.6 (4)
<i>Z</i>	4
Radiation type	Mo Kα (λ = 0.71073 Å)
μ (mm ⁻¹)	0.48
Crystal size (mm)	0.34 × 0.14 × 0.09
Diffractometer	Oxford Diffraction, Xcalibur PX
Absorption correction	Analytical
<i>T_{min}</i> , <i>T_{max}</i>	0.904, 0.969
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	9719, 2221, 1956
<i>R_{int}</i>	0.022
(sin θ/λ) _{max} (Å ⁻¹)	0.703
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.020, 0.060, 1.07
No. of reflections	2221
No. of parameters	140
No. of restraints	0
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.32, -0.32

Electron diffraction (3D-ED) for Na₄(P₂O₆)

Electron diffraction data for Na₄(P₂O₆) were collected using a Rigaku Synergy-ED diffractometer equipped with a Rigaku HyPix-ED detector optimised for electron detection and LaB₆ electron source at 200 kV.^{S7} Data collections, cell refinements, data reductions and analysis were carried out with *CrysAlisPro*.^{S3} The single dataset was collected with a wavelength of 0.0251 Å at ambient temperature and in a vacuum. The shutterless data collection was performed with a continuous crystal rotation method (3D-ED/MED) at the 645 mm detector distance. The dataset contains 600 frames, which were saved with a scan width of 0.2° and an exposure time of 0.4 seconds. Frame scaling and empirical absorption correction were applied for the final data. The structure was solved with intrinsic phasing (*SHELXT*^{S8}), and refined with kinematic approximation and extinction correction model, using *SHELXL*^{S6} in Olex2.^{S5} For experimental details see Table S2 in Supporting Information.

Table S2. Electron diffraction experimental details for Na₄(P₂O₆)

CSD Deposition Number	2246554
Chemical formula	Na ₄ O ₆ P ₂
<i>M_r</i> (g mol ⁻¹)	249.90
Crystal system, space group	Trigonal, <i>P</i> ³ ₁ <i>c</i> (No. 163)
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.30(15), 5.30(15), 12.0(2)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	90, 90, 120
<i>V</i> (Å ³)	291(17)
<i>Z</i>	2
Radiation type	200 kV electron beam (λ = 0.0251 Å)
<i>θ</i> range (°)	0.120–0.897
<i>R</i> ₁	0.101
<i>wR</i> ₂	0.271

Powder X-ray diffraction (PXRD) and variable-temperature PXRD (VT PXRD)

PXRD analyses were carried out on a Bruker D8 ADVANCE diffractometer equipped with copper X-ray radiation ($\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$) and a VÅNTEC-1 detector. Data were collected at room temperature in the 2θ range 5-60°. The experimental diffraction patterns were compared with theoretical patterns obtained from X-ray data of monocrystals using the Rietveld method with the use of HighScore Plus.⁵⁹

The data for Rietveld refinement of $\text{Na}_4(\text{P}_2\text{O}_6)$ was collected on PANalytical X'Pert Pro θ - 2θ diffractometer using β -filtered Cu $K\alpha$ radiation in the 2θ range of 10-120°, scan step 0.026° (for details see Table S3). Background was fitted as 8-parameter polynomial. Peak shape was approximated with Pseudo Voigt profile function along with two-parameter FCJ asymmetry. Scale factor and specimen displacement were refined. The coordinates (with special position restraints) and isotropic B-factors of all atoms were refined.

Variable-temperature PXRD analyses of $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ samples were performed on an X-ray powder diffractometer X'Pert Pro from PANalytical with Anton Paar HTK 1200N high-temperature chamber. Data were collected in the 2θ range of 11-70°, every 10 K in 298-408 K.

Table S3. Powder diffraction experimental details for $\text{Na}_4(\text{P}_2\text{O}_6)$

CSD Deposition Number	2246555
Chemical formula	$\text{Na}_4\text{O}_6\text{P}_2$
M_r (g mol^{-1})	249.90
Crystal system, space group	Trigonal, $P\bar{3}1c$ (No. 163)
Temperature (K)	293
a, b, c (\AA)	5.48954(4), 5.48954(4), 12.19461(8)
α, β, γ ($^\circ$)	90, 90, 120
V (\AA^3)	318.252(5)
Z	2
Radiation type	Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$)
d-space range (\AA)	0.891–6.073
χ^2	8.70
R_p	0.034
R_{wp}	0.045

Thermal analysis (TG-DSC) for $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$

Thermogravimetric TG-DSC analysis of $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$ (26.982 mg) was performed with the use of a Mettler-Toledo TGA/DSC 3+ instrument in the temperature range 303-1073 K with a ramp rate of 10 K min^{-1} . The scans were performed in flowing nitrogen (flow rate: $3 \text{ dm}^3 \text{ h}^{-1}$).

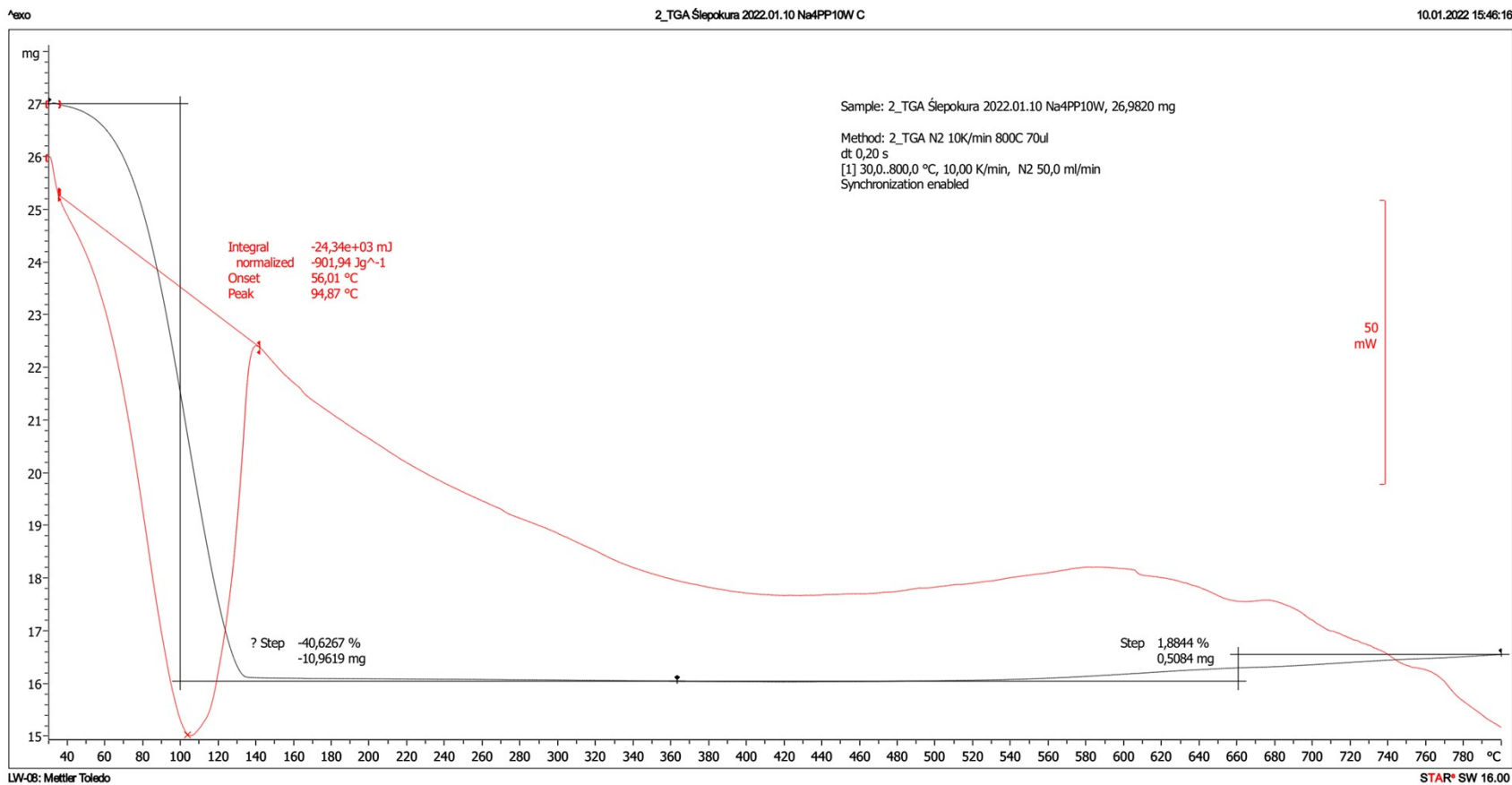


Figure S4. TG-DSC of $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$ (m = 26.982 mg).

Variable-temperature optical microscopy

Variable-temperature microscopy was performed in polarized light using an Olympus BX53 microscope equipped with a Linkam THMS 600 temperature adapter (78-873 K) and CCD XC50 video camera.

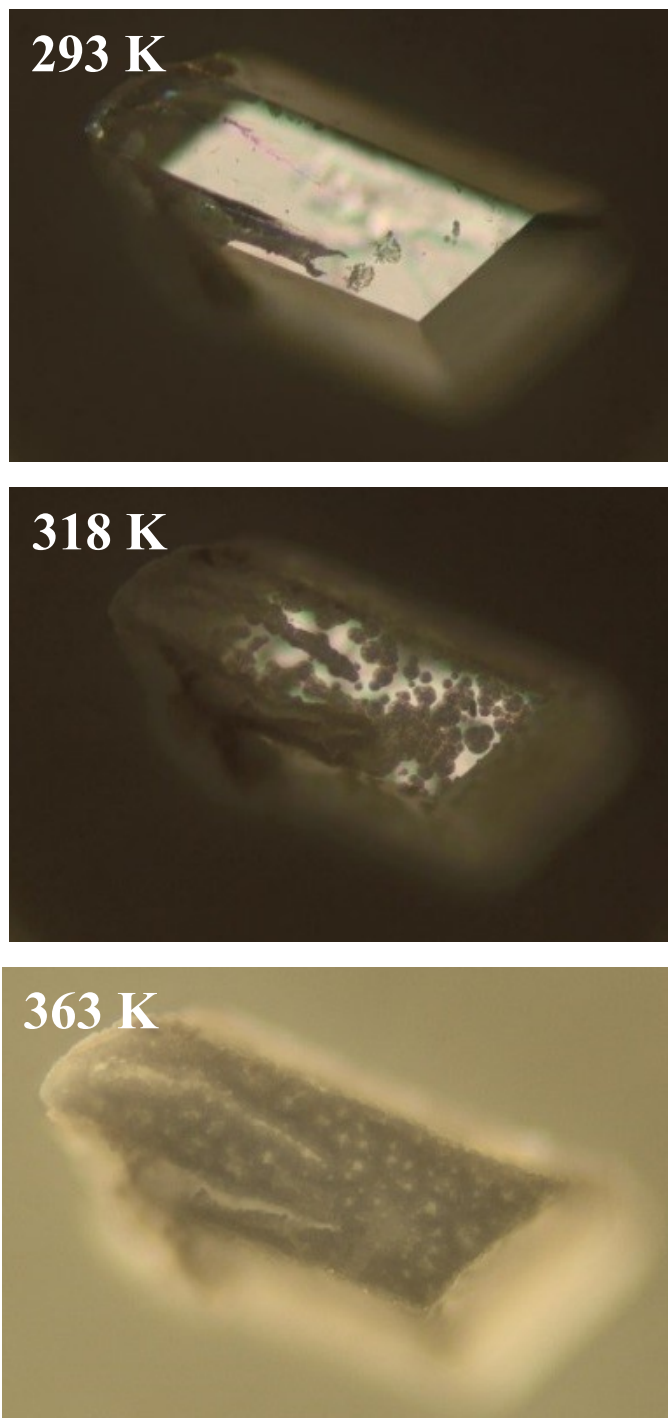


Figure S5. Variable-temperature microscopy of $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ in 293-363 K range.

Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX)

The electron microscopy imaging of the sample and its elemental composition were studied using Field Emission Scanning Electron Microscope (FE-SEM) FEI Nova NanoSEM 230 along with energy dispersive X-ray spectrometer (EDAX Genesis XM4).

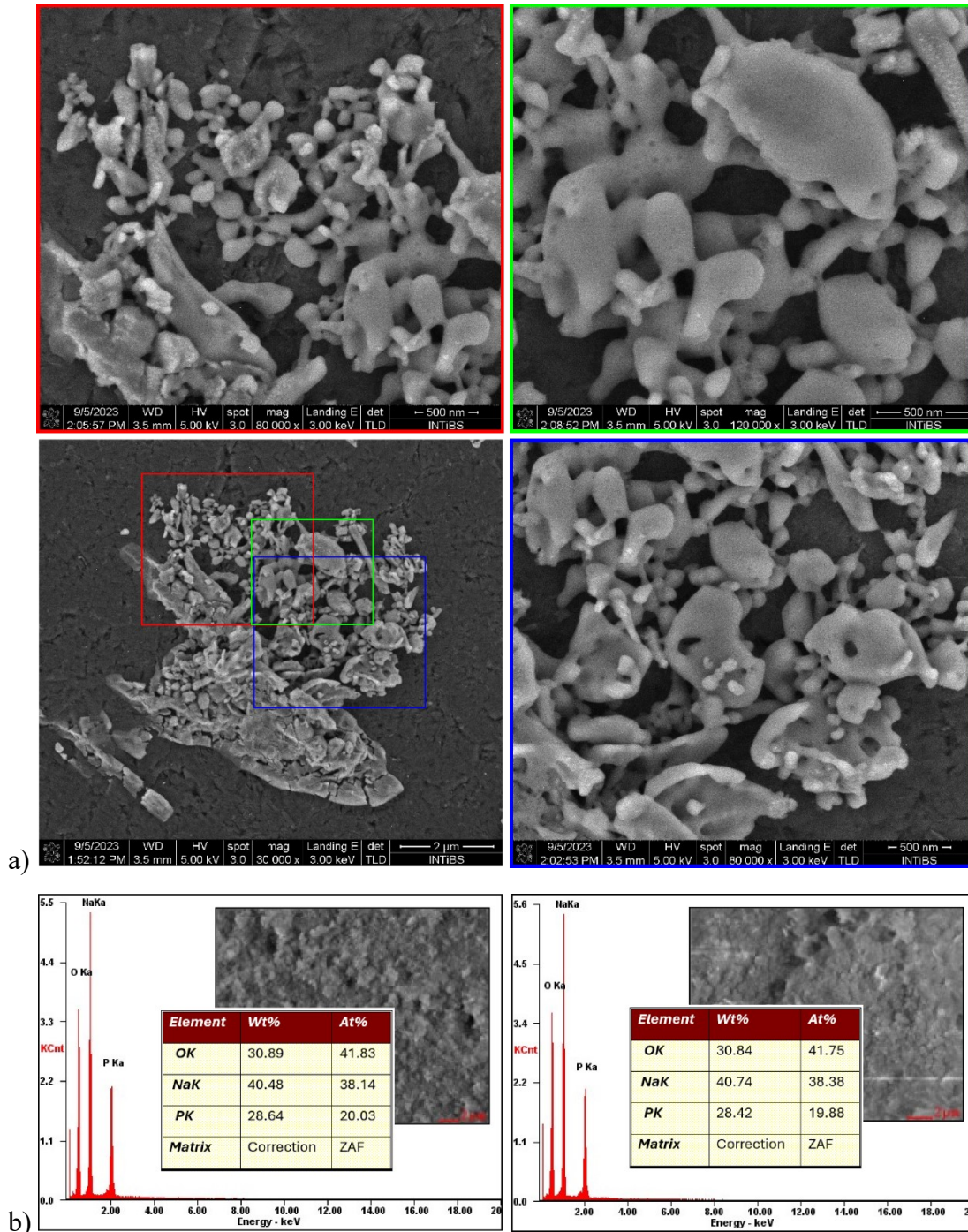


Figure S6. SEM images (a) and EDS analysis (b) of $\text{Na}_4(\text{P}_2\text{O}_6)$. Theoretical content by mass: Na 36.8%, P 24.79% and O 38.41%.

Electrical measurements for Na₄(P₂O₆)

The electrical measurements were performed between 300 and 540 K using an Agilent E4980A Precision LCR Meter in the frequency range between 135 Hz and 2 MHz for parallel C_p - D equivalent circuit (Fig. S7 and S8). The ac conductivity was calculated as:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta = \omega \varepsilon_0 \frac{C_p}{C_0} D \quad (x)$$

where ε_0 – the vacuum permittivity; ε' – real part of complex dielectric permittivity; C_p measured capacitance of sample, C_0 – geometrical capacitance of sample; $\tan \delta = D$ – loss tangent and $\omega = 2\pi f$ (f [Hz]) is the angular frequency.

The polycrystalline material was used in the form of pressed pellets. The diameter of the pellets was 5 mm, and the thickness was 0.8-1.2 mm. The overall error in estimating the AC conductivity value was less than 5%. The pellet surfaces were coated with gold electrodes with a mask using a sputter coating system (Quorum Q150T S). The electric measurements were carried out in a controlled atmosphere (N₂).

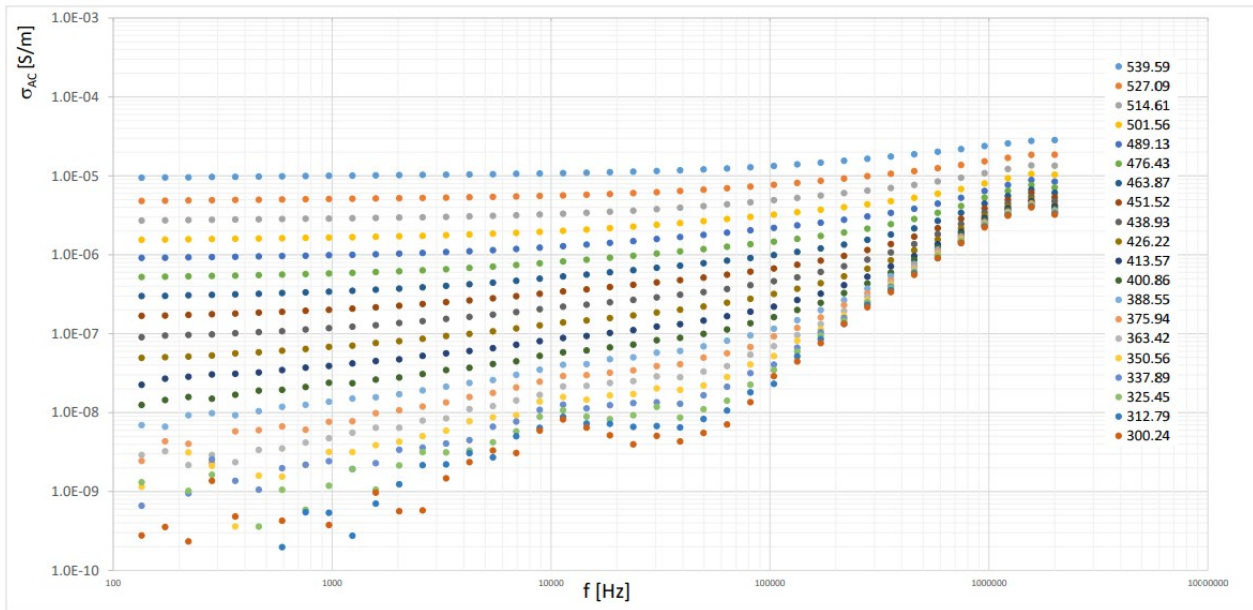


Figure S7. Conductivity (AC) versus frequency dependence for Na₄(P₂O₇) (S/m vs Hz) in the temperature range 300–540 K.

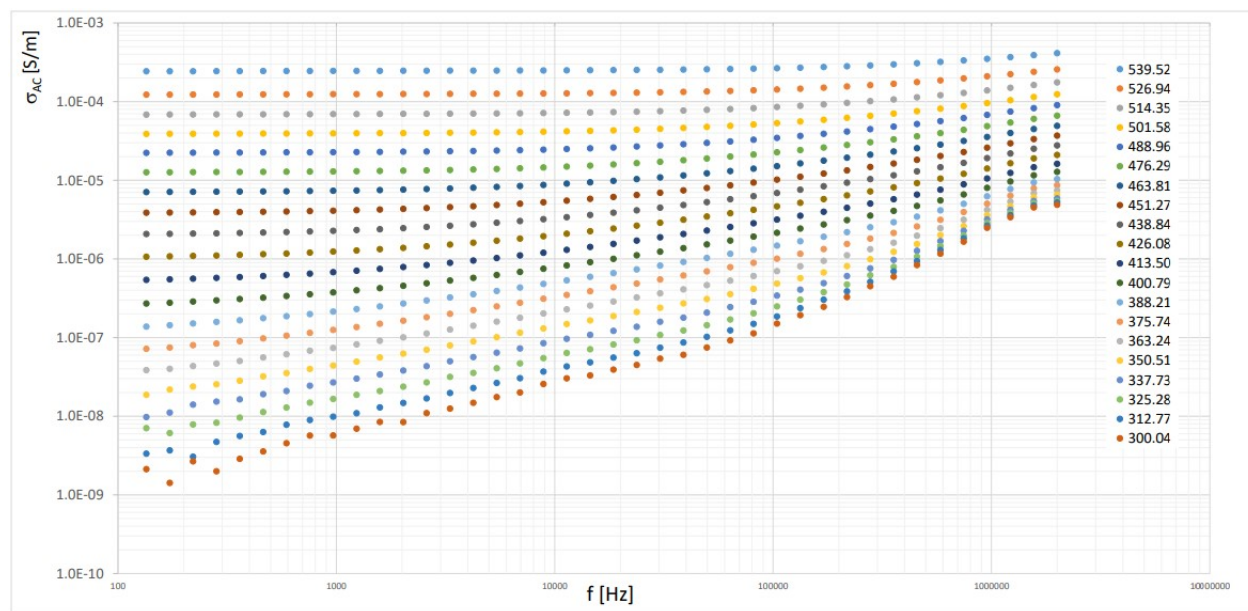


Figure S8. Conductivity (AC) versus frequency dependence for $\text{Na}_4(\text{P}_2\text{O}_6)$ (S/m vs Hz) in the temperature range 300–540 K.

Crystallographic data deposition and analysis

Crystallographic data and structure refinement parameters for $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_6)$ (SC-XRD, 3D-ED and PXRD) are summarized in Tables S1-S3 and the crystallographic information files (CIFs) deposited via the joint CCDC/FIZ Karlsruhe deposition service (CSD deposition Nos. 2246554-2246556) and provided as Supporting Data.

All figures were made using the DIAMOND program.^{S10} The coordination geometries around the tri-, penta- and hexacoordinate sodium centres were analysed with the use of *SHAPE* program.^{S11}

Asymmetric units of the crystals

The asymmetric units of the crystals contain Na^+ cations and $\text{P}_2\text{O}_6^{4-}$ hypodiphosphate tetraanions. In the decahydrate crystal water molecules are also present (Figure S4). As given in Table S4, two sodium cations in $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ lie in general positions, while all Na^+ ions in $\text{Na}_4(\text{P}_2\text{O}_6)$ lie in special positions – on threefold axis, on threefold inversion axis or at 32. Hypodiphosphate $\text{P}_2\text{O}_6^{4-}$ ions also lie in special positions – on twofold axis in $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ or at 32 in $\text{Na}_4(\text{P}_2\text{O}_6)$. Water molecules in hydrated crystal are located in general positions.

Table S4. Contents of asymmetric units of crystals $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_6)$.

Formula	Na^+ cations	PP anions	H_2O
$\text{Na}_4(\text{P}_2\text{O}_6)$	$2 \times 1/6 + 1/3$ Na1 [32], Na2 [$\bar{3}$], Na3 [3]	$1/6 \text{ P}_2\text{O}_6^{4-}$ [32]	–
$\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$	2	$0.5 \text{ P}_2\text{O}_6^{4-}$ [2]	5

[2], [3], [$\bar{3}$] and [32] denote symmetry of special position on which an ion lies

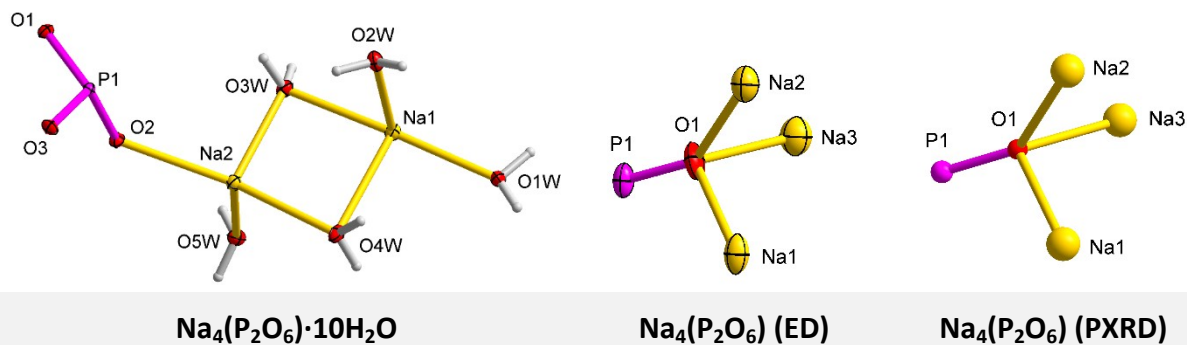
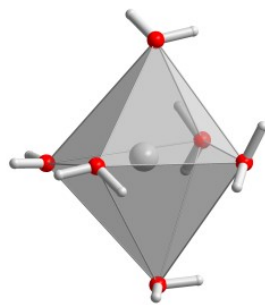
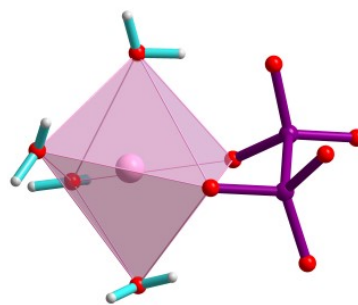


Figure S9. Asymmetric units of crystals $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_6)$ showing the atom-numbering schemes. Displacement ellipsoids in $\text{Na}_4(\text{P}_2\text{O}_6)\cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_6)$ (ED) are shown at the 50% probability level. For $\text{Na}_4(\text{P}_2\text{O}_6)$ (PXR) thermal parameters were refined in isotropic mode.

Coordination environments of sodium cations

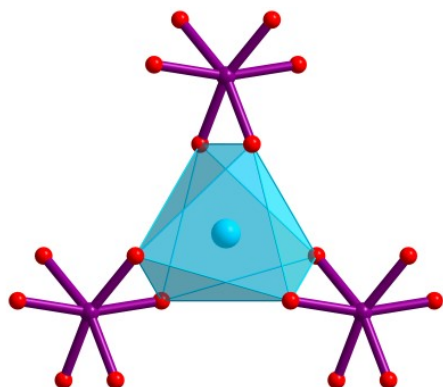


Na1, CN = 6
[Na(H₂O)₆]

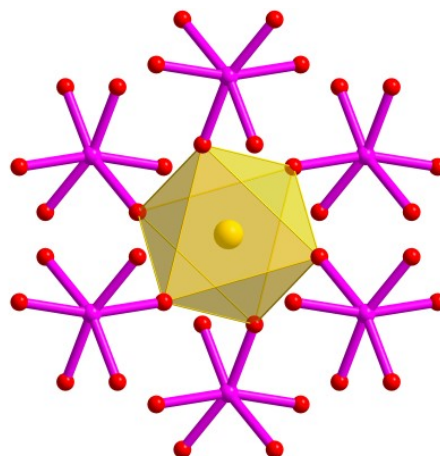


Na2, CN = 6
[Na(PP^b)(H₂O)₄]

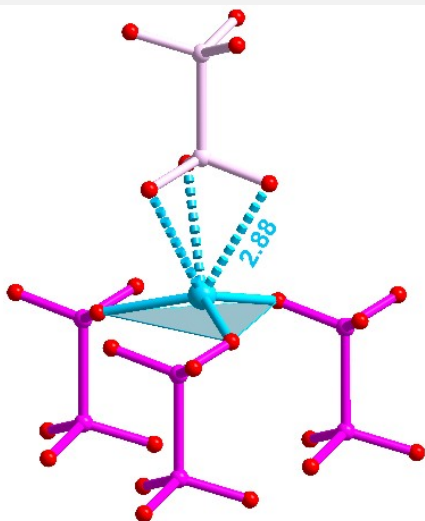
Figure S10. Environment of Na cations (CN = 6) in Na₄(P₂O₆)·10H₂O. Octahedral [Na(H₂O)₆] and [Na(PP^b)(H₂O)₄] units are shown. Hypodiphosphate H atoms are omitted for clarity. PP^b – bidentate anions.



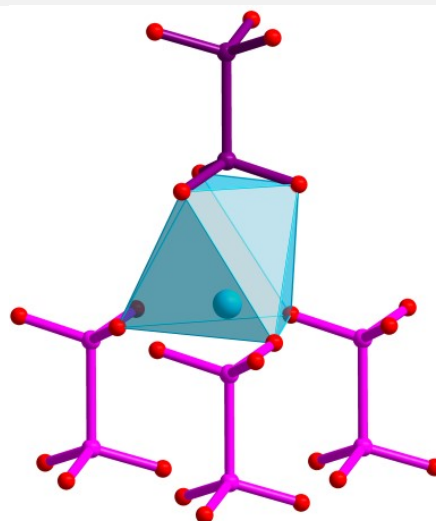
Na1, CN = 6
highly deformed octahedral [Na(PP^b)₃]



Na2, CN = 6
octahedral [Na(PP)₆]



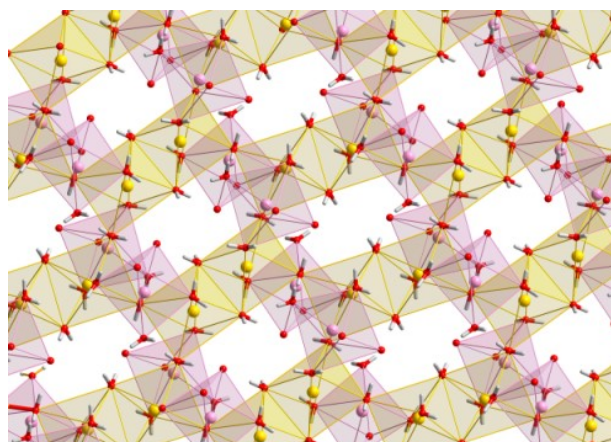
Na3, CN = 3
pyramidal (vacant tetrahedral) [Na(PP)₃]



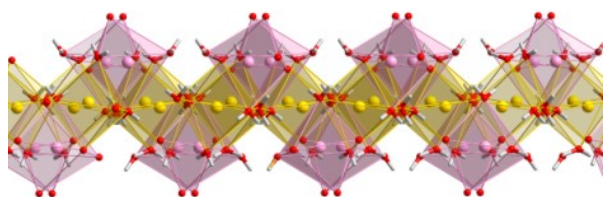
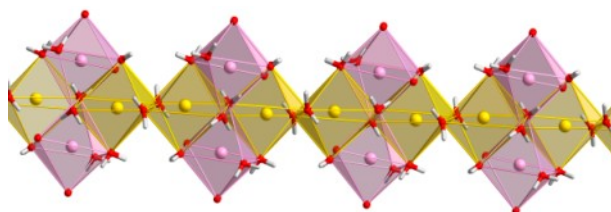
Na3, CN = 3+3
highly deformed octahedral [Na(PP^t)(PP)₃]

Figure S11. Environment of Na cations (CN = 3, 3+3 or 6) in Na₄(P₂O₆). Na3 cation shown as considered both as three-coordinated pyramidal (vacant tetrahedral; Na...O distances are given in Å.) [Na(PP)₃] unit, and highly deformed octahedral [Na(PP^t)(PP)₃] unit. PP – monodentate anion (pink), PP^b and PP^t – bidentate and tridentate anions, respectively (violet).

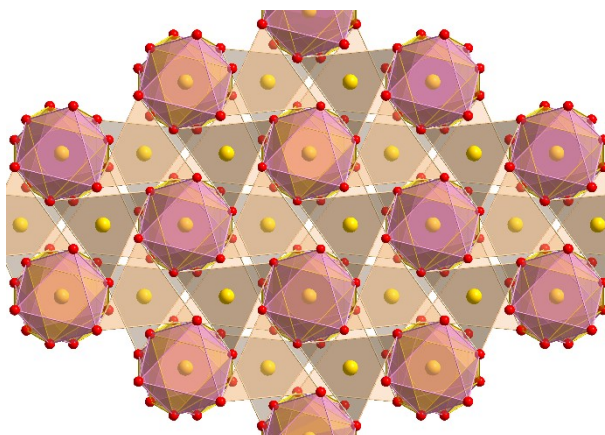
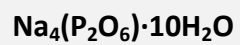
Cationic substructures



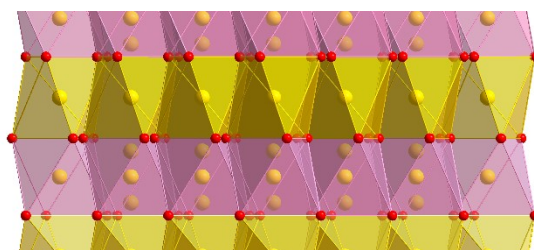
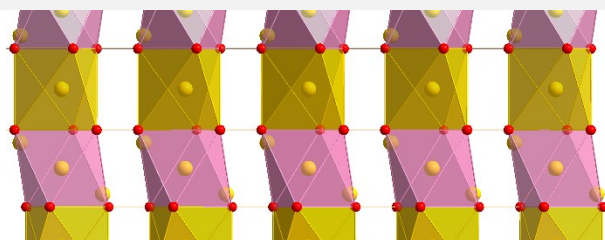
top view



side views



top view



side view

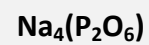
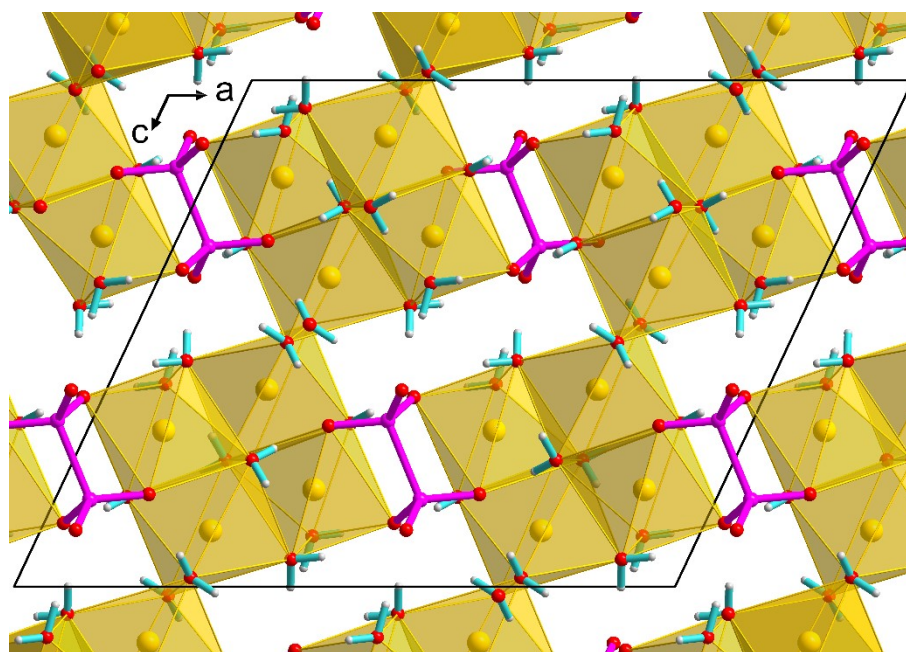
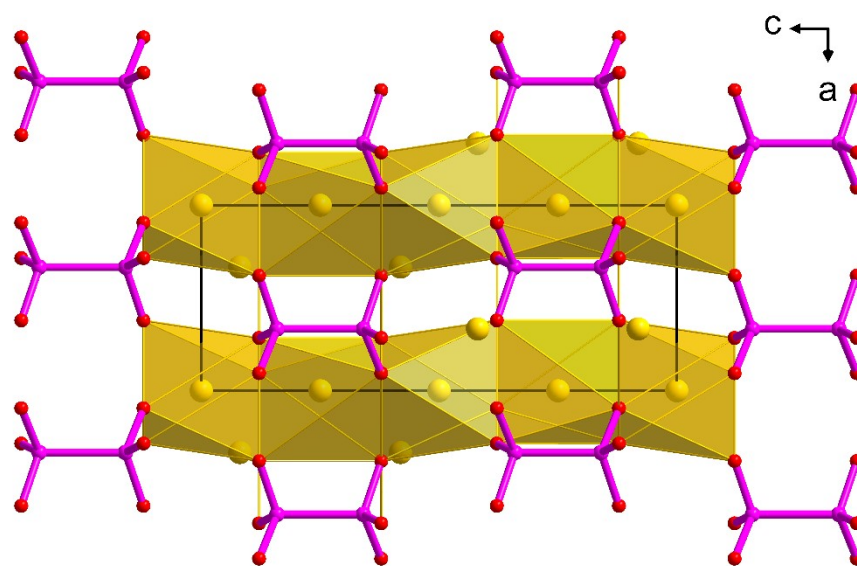


Figure S12. Two-dimensional cationic substructure in $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$ and three-dimensional cationic substructure in $\text{Na}_4(\text{P}_2\text{O}_6)$.

Crystal packing diagrams for the crystals



$\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$



$\text{Na}_4(\text{P}_2\text{O}_6)$

Figure S13. Crystal packing diagrams of crystals $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_6)$. Sodium cations are shown as orange spheres.

Coordination environments of hypodiphosphate anions

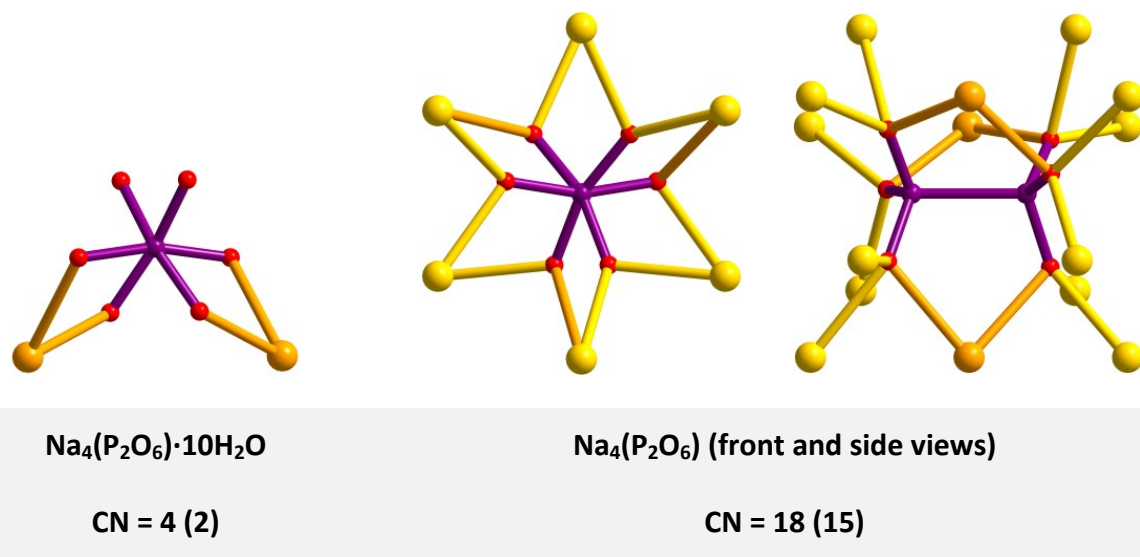


Figure S14. The coordination environment of the hypodiphosphate anions in $\text{Na}_4(\text{P}_2\text{O}_6) \cdot 10\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{O}_6)$ (viewed down the P–P bond). CN – coordination number. The number of Na cations (yellow – bound in monodentate manner, and orange – di- and tridentate) surrounding the PP anion is given in parentheses.

Migration pathways in $\text{Na}_4(\text{P}_2\text{O}_7)$

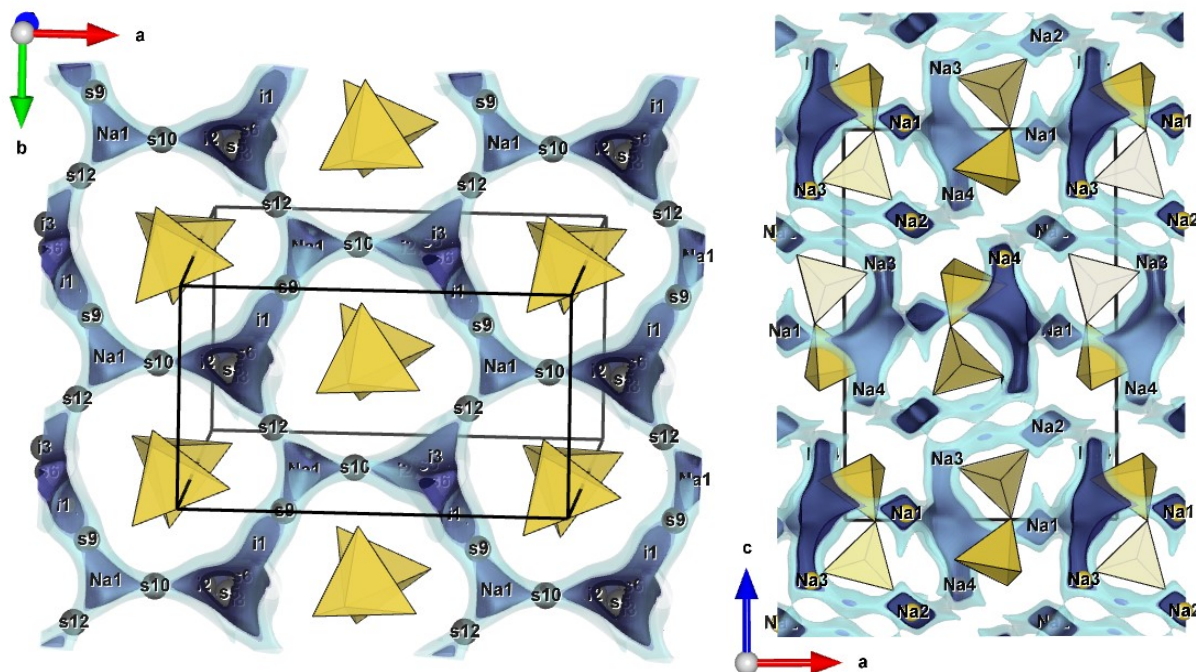


Figure S15. Top and side views of possible migration routes in $\text{Na}_4(\text{P}_2\text{O}_7)$.^{S12}

Energy profile for ion migration in Na₄(P₂O₇)

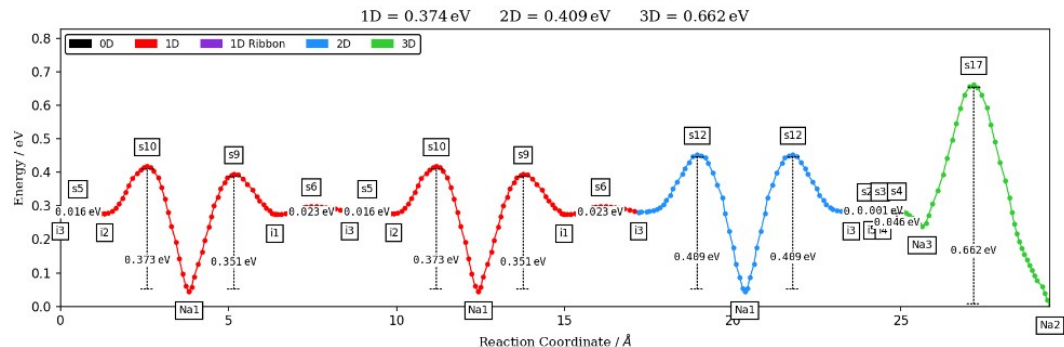


Figure S16. Top and side views of possible migration routes in Na₄(P₂O₇).

Geometric parameters for the crystals

Table S5. Selected geometric parameters (Å, °) for P₂O₆⁴⁻ anions in Na₄(P₂O₆)·10H₂O and Na₄(P₂O₆) (PXRD).

	Na ₄ (P ₂ O ₆)·10H ₂ O		Na ₄ (P ₂ O ₆)
P1—P1 ^{iv}	2.1949(8)	P1—P1 ⁱ	2.2048(7)
P1—O1	1.5283(7)	P1—O1	1.5334(5)
P1—O2	1.5323(7)	P1—O1 ⁱⁱ	1.5334(5)
P1—O3	1.5351(7)	P1—O1 ⁱⁱⁱ	1.5334(5)
O1—P1—P1 ^{iv}	107.06(3)	O1—P1—P1 ⁱ	107.46(3)
O2—P1—P1 ^{iv}	101.31(3)	O1 ⁱⁱ —P1—P1 ⁱ	107.46(3)
O3—P1—P1 ^{iv}	112.33(3)	O1 ⁱⁱⁱ —P1—P1 ⁱ	107.46(3)
O1—P1—O2	111.16(4)	O1—P1—O1 ⁱⁱ	111.41(3)
O1—P1—O3	112.81(4)	O1—P1—O1 ⁱⁱⁱ	111.41(3)
O2—P1—O3	111.53(4)	O1 ⁱⁱ —P1—O1 ⁱⁱⁱ	111.41(3)
O1—P1—P1 ^{iv} —O1 ^{iv}	-164.08(6)	O1—P1—P1 ⁱ —O1 ^{iv}	161.77(4)
O2—P1—P1 ^{iv} —O1 ^{iv}	-47.56(4)	O1—P1—P1 ⁱ —O1 ⁱ	41.77(4)
O3—P1—P1 ^{iv} —O1 ^{iv}	71.56(4)	O1—P1—P1 ⁱ —O1 ^v	-78.23(4)
O1—P1—P1 ^{iv} —O2 ^{iv}	-47.56(4)	O1 ⁱⁱ —P1—P1 ⁱ —O1 ^{iv}	41.77(4)
O2—P1—P1 ^{iv} —O2 ^{iv}	68.95(6)	O1 ⁱⁱ —P1—P1 ⁱ —O1 ⁱ	-78.23(4)
O3—P1—P1 ^{iv} —O2 ^{iv}	-171.92(4)	O1 ⁱⁱ —P1—P1 ⁱ —O1 ^v	161.77(4)
O1—P1—P1 ^{iv} —O3 ^{iv}	71.56(4)	O1 ⁱⁱⁱ —P1—P1 ⁱ —O1 ^{iv}	-78.23(4)
O2—P1—P1 ^{iv} —O3 ^{iv}	-171.92(4)	O1 ⁱⁱⁱ —P1—P1 ⁱ —O1 ⁱ	161.77(4)
O3—P1—P1 ^{iv} —O3 ^{iv}	-52.80(6)	O1 ⁱⁱⁱ —P1—P1 ⁱ —O1 ^v	41.77(4)

Symmetry code for Na₄(P₂O₆)·10H₂O: (iv) -x+1, y, -z+1/2.

Symmetry codes for Na₄(P₂O₆): (i) y-x, y, -z+1/2; (ii) -y+1, x-y+1, z; (iii) y-x, -x+1, z;

(iv) -y+1, -x+1, -z+1/2; (v) x, x-y+1, -z+1/2.

Table S6. Selected Na–O and Na⋯Na distances (Å) in Na₄(P₂O₆)·10H₂O and Na₄(P₂O₆) (PXRD).

Na ₄ (P ₂ O ₆)·10H ₂ O			
Na1—O1W	2.2455(9)	Na2—O2	2.3854(9)
Na1—O3W	2.3276(9)	Na2—O5W	2.3880(9)
Na1—O2W ⁱ	2.3839(9)	Na2—O1 ^{iv}	2.5243(8)
Na1—O2W	2.3929(9)		
Na1—O4W	2.6189(9)	Na1⋯Na2	3.2337(9)
Na1—O4W ⁱⁱ	2.6609(9)	Na1⋯Na1 ⁱ	3.3637(9)
Na2—O3W	2.3390(9)	Na1⋯Na2 ⁱⁱ	3.4388(6)
Na2—O4W	2.3822(9)	Na2⋯Na1 ⁱⁱⁱ	3.4387(7)
Na2—O1W ⁱⁱⁱ	2.3824(9)		
Na ₄ (P ₂ O ₆)			
Na1—O1	2.4419(7)	Na1⋯Na2	3.0487(0)
Na1—O1 ^{i,ii,iii,iv,v}	2.4419(7)	Na1⋯Na2 ^v	3.0487(0)
Na2—O1	2.3939(7)	Na1⋯Na3	3.7791(3)
Na2—O1 ^{ii,iv,vi,vii,viii}	2.3939(7)	Na1⋯Na3 ^{v,xiii,xiv}	3.7791(3)
Na3—O1	2.2883(7)	Na2⋯Na3	3.3205(1)
Na3—O1 ^{ix,x}	2.2883(7)	Na2⋯Na3 ^{xi,xv}	3.3205(1)
Na3—O1 ^{vii,xi,xii}	2.8764(9)	Na3⋯Na1 ^{xi,xvi,xvii}	3.7791(3)
		Na3⋯Na2 ^{xvi}	3.3205(1)
		Na3⋯Na3 ^{xi,xviii,xix}	3.7375(4)

Symmetry codes for Na₄(P₂O₆)·10H₂O: (i) $-x+3/2, -y+3/2, -z+1$; (ii) $-x+3/2, y+1/2, -z+1/2$; (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $-x+1, y, -z+1/2$.

Symmetry codes for Na₄(P₂O₆): (i) $y-x, y, -z+1/2$; (ii) $y-x, -x, z$; (iii) $x, -y+x, -z+1/2$; (iv) $-y, -y+x, z$; (v) $-y, -x, -z+1/2$; (vi) $-x, -y, -z$; (vii) $-y+x, x, -z$; (viii) $y, y-x, -z$; (ix) $-x+y-1, -x, z$; (x) $-y, x-y+1, z$; (xi) $-x, -y+1, -z$; (xii) $y-1, -x+y, -z$; (xiii) $-y, -x-1, -z+0.5$; (xiv) $-y+1, -x, -z+0.5$; (xvi) $x-1, y, z$; (xvii) $x, y+1, z$; (xviii) $-x-1, -y, -z$; (xix) $-x-1, -y+1, -z$;

Continuous Shape Measurements (CShMs) for Na⁺ cations in the crystals

Table S7. Continuous Shape Measurements (CShMs) for Na⁺ cations in [NaO₆] and [NaO₃] polyhedra in the crystals of Na₄(P₂O₆)·10H₂O and Na₄(P₂O₆). Structure deviation from an ideal shape of a polyhedron obtained by SHAPE program.^{S11}

CN = 6, [NaO ₆]	JPPY-6 ^(a)	TPR-6 ^(a)	OC-6 ^(a)	PPY-6 ^(a)	HP-6 ^(a)
Na ₄ (P ₂ O ₆), Na1	24.657	4.565	4.235	20.765	33.153
Na ₄ (P ₂ O ₆), Na2	33.004	15.444	0.285	29.662	31.798
Na ₄ (P ₂ O ₆), Na3	34.106	17.308	5.277	30.226	34.978
Na ₄ (P ₂ O ₆)·10H ₂ O, Na1	28.782	12.485	0.805	25.937	31.786
Na ₄ (P ₂ O ₆)·10H ₂ O, Na2	26.206	11.682	1.571	22.100	32.732
CN = 3, [NaO ₃]	mvOC-3 ^(b)	fvOC-3 ^(b)	vT-3 ^(b)	TP-3 ^(b)	
Na ₄ (P ₂ O ₆), Na3	10.519	5.185	0.420	1.208	

^(a) Ideal structures for [NaO₆]: JPPY-6 (C_{5v}) – Johnson pentagonal pyramid, J2, TPR-6 (D_{3h}) – trigonal prism, OC-6 (O_h) – octahedron, PPY-6 (C_{5v}) – pentagonal pyramid, HP-6 (D_{6h}) – hexagon.
^(b) Ideal structures for [NaO₃]: mvOC-3 (C_{2v}) – mer-trivacant octahedron (T-shape), fvOC-3 (C_{3v}) – fac-trivacant octahedron, vT-3 (C_{3v}) – pyramid (vacant tetrahedron), TP-3 (D_{3h}) – trigonal planar.

Hydrogen-bond geometry for the crystal of Na₄(P₂O₆)·10H₂O

Table S8. Hydrogen-bond geometry (Å, °) for Na₄(P₂O₆)·10H₂O.

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H2W···O2 ⁱⁱ	0.812(19)	2.237(17)	2.8594(11)	133.7(15)
O1W—H1W···O2 ^v	0.837(18)	1.815(18)	2.6470(11)	172.5(17)
O2W—H3W···O1 ^{iv}	0.813(17)	1.993(17)	2.7917(12)	167.1(15)
O2W—H4W···O3 ^{vi}	0.836(19)	2.200(19)	2.9967(13)	159.3(16)
O3W—H5W···O3 ^{vii}	0.878(17)	1.896(17)	2.7701(10)	173.7(15)
O3W—H6W···O2 ^{iv}	0.866(17)	1.912(17)	2.7740(10)	173.5(15)
O4W—H7W···O1 ^{viii}	0.802(18)	1.889(18)	2.6886(11)	175.0(17)
O4W—H8W···O5W ⁱⁱⁱ	0.838(17)	2.035(17)	2.8616(12)	168.7(15)
O5W—H9W···O3 ^{ix}	0.852(17)	2.009(17)	2.8606(11)	179.0(16)
O5W—H10W···O3 ^x	0.821(18)	2.036(19)	2.8542(11)	174.7(16)

Symmetry codes: (ii) $-x+3/2, y+1/2, -z+1/2$; (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $-x+1, y, -z+1/2$; (v) $x+1/2, -y+3/2, z+1/2$; (vi) $x+1/2, -y+1/2, z+1/2$; (vii) $-x+1, y+1, -z+1/2$; (viii) $x+1/2, y+1/2, z$; (ix) $-x+1, -y+1, -z$; (x) $x, y+1, z$.

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