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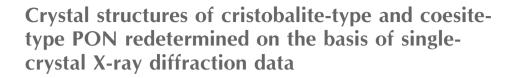
Acta Cryst E

CRYSTALLOGRAPHIC COMMUNICATIONS

Crystal structures of cristobalite-type and coesite-type PON redetermined on the basis of single-crystal X-ray diffraction data
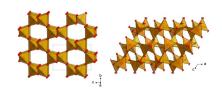
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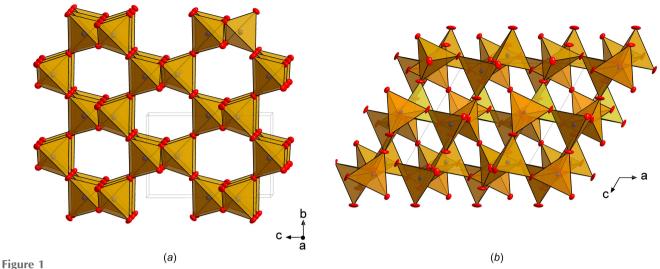
Hitherto, phosphorus oxonitride (PON) could not be obtained in the form of single crystals and only powder diffraction experiments were feasible for structure studies. In the present work we have synthesized two polymorphs of phosphorus oxonitride, cristobalite-type (cri-PON) and coesite-type (coe-PON), in the form of single crystals and reinvestigated their crystal structures by means of in house and synchrotron single-crystal X-ray diffraction. The crystal structures of cri-PON and coe-PON are built from PO_2N_2 tetrahedral units, each with a statistical distribution of oxygen and nitrogen atoms. The crystal structure of the coe-PON phase has the space group $C2/c$ with seven atomic sites in the asymmetric unit [two P and three (N,O) sites on general positions, one (N,O) site on an inversion centre and one (N,O) site on a twofold rotation axis], while the cri-PON phase possesses tetragonal $I\bar{4}2d$ symmetry with two independent atoms in the asymmetric unit [the P atom on a fourfold inversion axis and the (N,O) site on a twofold rotation axis]. In comparison with previous structure determinations from powder data, all atoms were refined with anisotropic displacement parameters, leading to higher precision in terms of bond lengths and angles.

1. Chemical context

The pseudo-binary system P_3N_5/P_2O_5 has been investigated intensively because the properties of related ceramic materials are promising for industrial applications. A mid-member of this system is phosphorus oxonitride (PON), whose chemical stability is essential for its use as an insulator or for fireproofing. This compound has attracted significant attention as a ternary base compound of electrolytes for rechargeable thin-film Li/Li-ion batteries. Phosphorus oxonitride is an isoelectronic analogue of silica (SiO_2) with the charge-balanced substitution $P^{5+} + N^{3-} = Si^{4+} + O^{2-}$. The crystal structures of the polymorphic forms of SiO_2 and PON are built of tetrahedral SiO_4 and PO_2N_2 units, respectively. At present, five modifications of PON have been identified. Four of them are isostructural to known silica polymorphs, viz. α-quartz- (Léger et al., 1999), β-cristobalite- (Léger et al., 2001), moganite- (Chateau et al., 1999) and coesite-type (Baumann et al., 2015). The fifth one, δ-PON, has a structure type different from any of the silica modifications (Baumann et al., 2012). A rich variety of polymorphs is a result of the many ways in which the tetrahedra can be linked to form corner-sharing networks. Most of the phases in the P_3N_5/P_2O_5 system are usually obtained either in an amorphous state or in the form of powders consisting of very small crystallites. We succeeded in

synthesizing single crystals of pure cristobalite- (*cri*) and coesite-type (*coe*) PON of a size suitable for single-crystal X-ray diffraction and report here the results of the structure refinements.

2. Structural commentary

The structure of *cri*-PON (Fig. 1*a*) can be derived from that of β-cristobalite by tilting each PO_2N_2 tetrahedron about the $\bar{4}$ axes alternately clockwise and anticlockwise. This leads to the lowering of symmetry from $Fd\bar{3}m$ to $I\bar{4}2d$, however, the topology remains the same. The length of the P—(O,N) bond in *cri*-PON is 1.5796 (10) Å, which is in a good agreement with the average of expected P—N (1.626 Å) and P—O (1.537 Å) distances (Huminicki & Hawthorne, 2002). All P—(O,N) distances within the PO_2N_2 units are equal, but there is a noticeable (O,N)—P—(O,N) angle variation between 107.86 (2) and 112.73 (5)° due to the compression of the tetrahedra along the *c*-axis direction.

The structure of *coe*-PON (Fig. 1*b*) is isotypic with coesite (SiO_2) (Angel *et al.*, 2003). The framework of *coe*-PON is constructed of four-member rings comprised of corner-sharing PO_2N_2 tetrahedra. These rings are linked in such a manner that crankshaft-like chains are formed. The average P—(O,N) distance in *coe*-PON (1.572 Å) is slightly shorter than that of 1.581 Å reported by Baumann *et al.* (2015) likely due to the difference in temperatures at which the experiments were conducted. The tetrahedra are irregularly distorted, with P—(O,N) distances varying between 1.5530 (9) and 1.588 (3) Å, and (O,N)—P—(O,N) angles between 106.79 (19) and 112.0 (2)°.

In comparison with the refinements from powder diffraction data (Léger *et al.*, 2001; Baumann *et al.*, 2015), single-crystal diffraction data revealed a detailed electron density map, which allowed us in addition to a substitutional O-N disorder, to detect a possible positional disorder (for details see *Refinement* section), which may affect physical properties of *coe*-PON.

3. Synthesis and crystallisation

Cristobalite-type PON was synthesized from phosphoric triamide by a two-step condensation process. $POCl_3$ (99%, Sigma Aldrich) was reacted with liquid NH_3 (5.0, Air Liquide) to yield a mixture of $PO(NH_2)_3$ and NH_4Cl, which was subsequently heated to 893 K for 5 h in a stream of dry ammonia. The amorphous reaction product was crystallized at 1023 K for 7 d in an evacuated fused silica ampoule, yielding pure cristobalite-type PON. Coesite-type PON was obtained by high-pressure/high-temperature reaction of *cri*-PON in a modified Walker-type multi-anvil apparatus. The starting material was tightly packed in a *h*-BN capsule, which was centered in a MgO:Cr octahedron (Ceramic Substrates & Components, Isle of Wight, UK) with an edge length of 10 mm. The latter was subsequently compressed between eight truncated tungsten carbide cubes (5 mm truncation edge length, Hawedia, Marklkofen, Germany) using a 1000 t hydraulic press (Voggenreiter, Mainleus, Germany). The sample was compressed to 15.5 GPa, the temperature raised to 1573 K within 15 min and held constant for 60 min. The sample was cooled by turning off the heating, decompressed and mechanically isolated.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Structure refinements of both *coe*-PON and *cri*-PON were performed using occupancies of oxygen and nitrogen atoms fixed to 0.5 for each site. As a result of the very similar scattering powers of N and O atoms, an attempt to refine the occupancies resulted in unreliable values with large standard uncertainties. The *cri*-PON crystal

Table 1
Experimental details.

	cri-PON	coe-PON
Crystal data		
Chemical formula	PON	PON
M_r	60.98	60.98
Crystal system, space group	Tetragonal, $I\bar{4}2d$	Monoclinic, $C2/c$
Temperature (K)	293	100
a, b, c (Å)	4.6135 (2), 4.6135 (2), 6.9991 (5)	6.9464 (6), 12.0340 (4), 6.9463 (5)
α, β, γ (°)	90, 90, 90	90, 119.914 (10), 90
V (Å³)	148.97 (2)	503.30 (7)
Z	4	16
Radiation type	Mo $K\alpha$	Synchrotron, $\lambda = 0.69428$ Å
μ (mm⁻¹)	1.24	1.35
Crystal size (mm)	$0.02 \times 0.02 \times 0.02$	$0.02 \times 0.02 \times 0.02$
Data collection		
Diffractometer	Bruker SMART APEX CCD	PILATUS@SNBL
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.791, 1.000	0.949, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	445, 92, 92	2415, 535, 469
R_{int}	0.016	0.038
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.666	0.640
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.016, 0.043, 1.45	0.037, 0.102, 1.05
No. of reflections	92	535
No. of parameters	8	57
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.21, −0.28	1.41, −0.54
Absolute structure	Refined as a perfect inversion twin.	–
Absolute structure parameter	0.5	–

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

was twinned by inversion with an equal amount of the two twin domains. The refinement of the *coe*-PON structure revealed a residual electron density peak of 1.41 e⁻·Å⁻³ at a distance 1.22 Å from atom P2 and 1.50, 1.65 and 1.65 Å from atoms O1, O2 and O5, respectively. This density may be explained by a static disorder of the P2 atom between two positions. The disorder is, however, too weak to give additional reliable residual density peaks for the assignments of oxygen and nitrogen atoms.

Acknowledgements

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Crystal structures of cristobalite-type and coesite-type PON redetermined on the basis of single-crystal X-ray diffraction data

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Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(cri-PON) Phosphorus oxonitride

Crystal data

NOP	$D_x = 2.719$ Mg m^{-3}
$M_r = 60.98$	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Tetragonal, $I\bar{4}2d$	Cell parameters from 431 reflections
$a = 4.6135$ (2) Å	$\theta = 5.3-28.2°$
$c = 6.9991$ (5) Å	$\mu = 1.24$ mm^{-1}
$V = 148.97$ (2) Å^3	$T = 293$ K
$Z = 4$	Prism, colourless
$F(000) = 120$	$0.02 \times 0.02 \times 0.02$ mm

Data collection

Three-circle diffractometer	445 measured reflections
Radiation source: rotating-anode X-ray tube, Rigaku Rotor Flex FR-D	92 independent reflections
	92 reflections with $I > 2\sigma(I)$
Detector resolution: 16.6 pixels mm^{-1}	$R_{int} = 0.016$
ω scans	$\theta_{max} = 28.3°$, $\theta_{min} = 5.3°$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)	$h = -5 \rightarrow 5$
	$k = -5 \rightarrow 6$
	$l = -5 \rightarrow 9$
$T_{min} = 0.791$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 0.0508P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.016$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.043$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$S = 1.45$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
92 reflections	Absolute structure: Refined as a perfect inversion twin.
8 parameters	Absolute structure parameter: 0.5
0 restraints	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component perfect inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
P	0.5000	0.5000	0.0000	0.0106 (3)	
N	0.3630 (5)	0.2500	0.1250	0.0155 (5)	0.5
O	0.3630 (5)	0.2500	0.1250	0.0155 (5)	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.0112 (4)	0.0112 (4)	0.0094 (4)	0.000	0.000	0.000
N	0.0151 (11)	0.0149 (12)	0.0165 (9)	0.000	0.000	0.0065 (10)
O	0.0151 (11)	0.0149 (12)	0.0165 (9)	0.000	0.000	0.0065 (10)

Geometric parameters (Å, º)

P—O[i]	1.5796 (10)	P—O[iii]	1.5796 (10)
P—N[i]	1.5796 (10)	P—N[iii]	1.5796 (10)
P—O[ii]	1.5796 (10)	P—N	1.5796 (10)
P—N[ii]	1.5796 (10)	N—P[iv]	1.5796 (10)
O[i]—P—N[i]	0.0	N[i]—P—N[iii]	107.86 (2)
O[i]—P—O[ii]	107.86 (2)	O[ii]—P—N[iii]	112.7
N[i]—P—O[ii]	107.86 (2)	N[ii]—P—N[iii]	112.73 (5)
O[i]—P—N[ii]	107.9	O[iii]—P—N[iii]	0.0
N[i]—P—N[ii]	107.86 (2)	O[i]—P—N	112.7
O[ii]—P—N[ii]	0.0	N[i]—P—N	112.73 (5)
O[i]—P—O[iii]	107.86 (2)	O[ii]—P—N	107.9
N[i]—P—O[iii]	107.86 (2)	N[ii]—P—N	107.86 (2)
O[ii]—P—O[iii]	112.73 (5)	O[iii]—P—N	107.9
N[ii]—P—O[iii]	112.73 (5)	N[iii]—P—N	107.86 (2)
O[i]—P—N[iii]	107.9	P—N—P[iv]	132.83 (16)

Symmetry codes: (i) −x+1, −y+1, z; (ii) y, −x+1, −z; (iii) −y+1, x, −z; (iv) x, −y+1/2, −z+1/4.

(coe-PON) Phosphorus oxonitride

Crystal data

NOP	c = 6.9463 (5) Å
M_r = 60.98	β = 119.914 (10)°
Monoclinic, $C2/c$	V = 503.30 (7) Å^3
a = 6.9464 (6) Å	Z = 16
b = 12.0340 (4) Å	$F(000)$ = 480

$D_x = 3.219$ Mg m^{-3}

Synchrotron radiation, $\lambda = 0.69428$ Å

Cell parameters from 1202 reflections

$\theta = 3.3$–$26.3°$

$\mu = 1.35$ mm^{-1}

$T = 100$ K

Prism, colourless

$0.02 \times 0.02 \times 0.02$ mm

Data collection

PILATUS@SNBL
    diffractometer

Radiation source: Beamline BM1A, SNBL
    ESRF, Grenoble, France

Detector resolution: 5.8 pixels mm^{-1}

φ scans

Absorption correction: multi-scan
    (*CrysAlis PRO*; Agilent, 2014)

$T_{min} = 0.949$, $T_{max} = 1.000$

2415 measured reflections

535 independent reflections

469 reflections with $I > 2\sigma(I)$

$R_{int} = 0.038$

$\theta_{max} = 26.4°$, $\theta_{min} = 3.3°$

$h = -8 \rightarrow 8$

$k = -15 \rightarrow 15$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.102$

$S = 1.05$

535 reflections

57 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 4.3556P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.41$ e Å^{-3}

$\Delta\rho_{min} = -0.53$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
P1	0.28266 (16)	0.09026 (8)	0.04006 (16)	0.0067 (4)	
P2	0.31812 (17)	0.35749 (7)	0.42525 (17)	0.0084 (4)	
N1	0.2117 (5)	0.4603 (2)	0.4818 (6)	0.0148 (8)	0.5
O1	0.2117 (5)	0.4603 (2)	0.4818 (6)	0.0148 (8)	0.5
N2	0.2500	0.2500	0.5000	0.0116 (10)	0.5
O2	0.2500	0.2500	0.5000	0.0116 (10)	0.5
N3	0.2322 (6)	0.3532 (3)	0.1704 (5)	0.0188 (8)	0.5
O3	0.2322 (6)	0.3532 (3)	0.1704 (5)	0.0188 (8)	0.5
N4	0.5000	0.1336 (3)	0.2500	0.0110 (10)	0.5
O4	0.5000	0.1336 (3)	0.2500	0.0110 (10)	0.5
N5	0.0792 (5)	0.1273 (3)	0.0656 (6)	0.0186 (8)	0.5
O5	0.0792 (5)	0.1273 (3)	0.0656 (6)	0.0186 (8)	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0054 (7)	0.0057 (6)	0.0070 (7)	0.0003 (3)	0.0016 (5)	0.0013 (3)

P2	0.0075 (7)	0.0071 (6)	0.0095 (7)	0.0000 (4)	0.0035 (5)	0.0011 (4)
N1	0.0191 (18)	0.0047 (15)	0.0250 (19)	0.0010 (12)	0.0142 (16)	−0.0018 (12)
O1	0.0191 (18)	0.0047 (15)	0.0250 (19)	0.0010 (12)	0.0142 (16)	−0.0018 (12)
N2	0.013 (2)	0.006 (2)	0.016 (2)	−0.0007 (16)	0.008 (2)	0.0032 (17)
O2	0.013 (2)	0.006 (2)	0.016 (2)	−0.0007 (16)	0.008 (2)	0.0032 (17)
N3	0.028 (2)	0.0177 (16)	0.0062 (18)	−0.0054 (14)	0.0048 (16)	0.0015 (13)
O3	0.028 (2)	0.0177 (16)	0.0062 (18)	−0.0054 (14)	0.0048 (16)	0.0015 (13)
N4	0.008 (2)	0.009 (2)	0.013 (2)	0.000	0.003 (2)	0.000
O4	0.008 (2)	0.009 (2)	0.013 (2)	0.000	0.003 (2)	0.000
N5	0.0034 (17)	0.0255 (18)	0.0213 (19)	0.0014 (13)	0.0020 (15)	−0.0079 (15)
O5	0.0034 (17)	0.0255 (18)	0.0213 (19)	0.0014 (13)	0.0020 (15)	−0.0079 (15)

Geometric parameters (Å, º)

P1—O3[i]	1.568 (3)	P2—O5[iii]	1.584 (3)
P1—N3[i]	1.568 (3)	P2—N5[iii]	1.584 (3)
P1—O1[ii]	1.573 (3)	P2—N1	1.588 (3)
P1—N1[ii]	1.573 (3)	N1—P1[iv]	1.574 (3)
P1—N5	1.574 (3)	N2—P2[v]	1.5530 (9)
P1—N4	1.5755 (17)	N3—P1[i]	1.568 (3)
P2—N2	1.5530 (9)	N4—P1[vi]	1.5755 (17)
P2—N3	1.562 (3)	N5—P2[vii]	1.584 (3)
O3[i]—P1—N3[i]	0.0	N2—P2—N3	110.10 (13)
O3[i]—P1—O1[ii]	109.55 (17)	N2—P2—O5[iii]	109.69 (13)
N3[i]—P1—O1[ii]	109.55 (17)	N3—P2—O5[iii]	112.0 (2)
O3[i]—P1—N1[ii]	109.55 (17)	N2—P2—N5[iii]	109.69 (13)
N3[i]—P1—N1[ii]	109.55 (17)	N3—P2—N5[iii]	112.0 (2)
O1[ii]—P1—N1[ii]	0.0	O5[iii]—P2—N5[iii]	0.0
O3[i]—P1—N5	109.7 (2)	N2—P2—N1	108.03 (12)
N3[i]—P1—N5	109.7 (2)	N3—P2—N1	110.13 (18)
O1[ii]—P1—N5	111.04 (17)	O5[iii]—P2—N1	106.79 (19)
N1[ii]—P1—N5	111.04 (17)	N5[iii]—P2—N1	106.79 (19)
O3[i]—P1—N4	107.83 (16)	P1[iv]—N1—P2	135.5 (2)
N3[i]—P1—N4	107.83 (16)	P2—N2—P2[v]	180.0
O1[ii]—P1—N4	111.09 (19)	P2—N3—P1[i]	148.5 (2)
N1[ii]—P1—N4	111.09 (19)	P1[vi]—N4—P1	141.3 (3)
N5—P1—N4	107.57 (15)	P1—N5—P2[vii]	141.3 (2)

Symmetry codes: (i) −*x*+1/2, −*y*+1/2, −*z*; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) *x*+1/2, −*y*+1/2, *z*+1/2; (iv) −*x*+1/2, *y*+1/2, −*z*+1/2; (v) −*x*+1/2, −*y*+1/2, −*z*+1; (vi) −*x*+1, *y*, −*z*+1/2; (vii) *x*−1/2, −*y*+1/2, *z*−1/2.