NPO

NPO.1 Zeolite framework type and topology

The designation of the framework type code (FTC) refers to the chemical composition of the type material oxo**N**itrido**P**hosphate with sequence number **O**ne [2003Cor1, 2004Cor1, 2004Cor2]. Its framework density of 21.7 T-atoms per 1000 Å^3 is higher than usually assumed for zeolite-type structures [2001Bae1]. However, its theoretical silica counterpart (Fig. NPO.1.1) has a density of 16 T-atoms per 1000 Å^3 as determined from DLS refinements. The framework structure (Fig. NPO.1.1) can be described as being built entirely from *bb44* ($3^2 6^3$) units as shown in Fig. NPO.1.2. Linkage of the *bb44* units yields the *kok* ($6^6 12^2$) units forming the 12-ring channels (**cnc** units, Fig. NPO.1.4) parallel **c**.

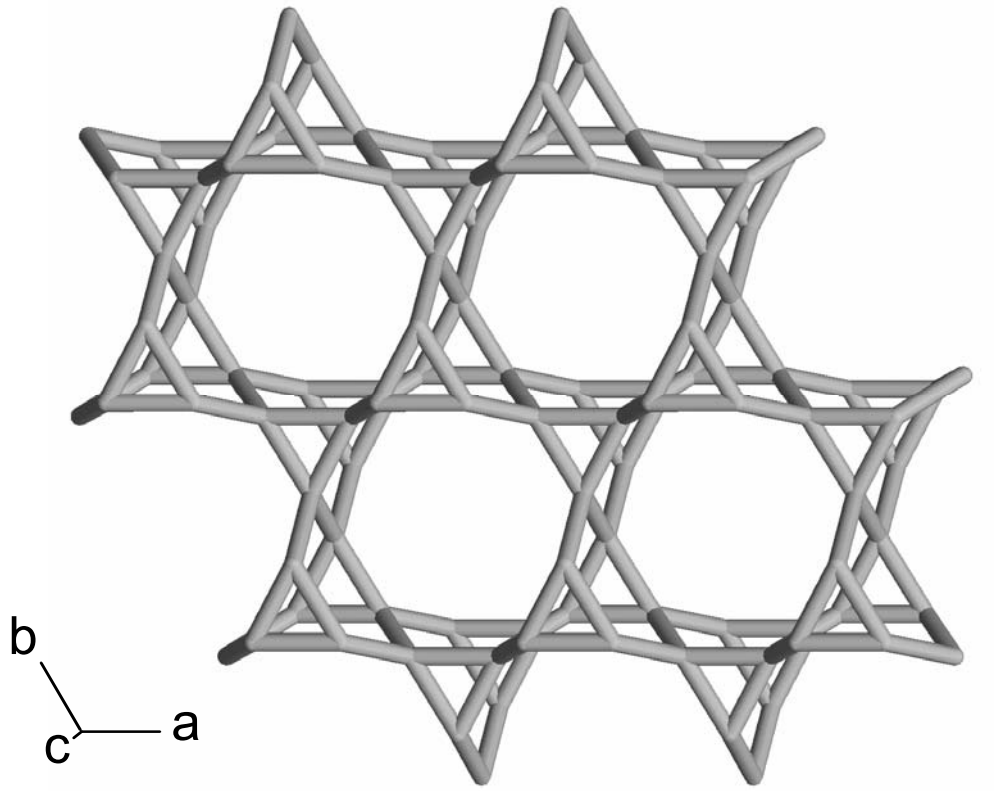
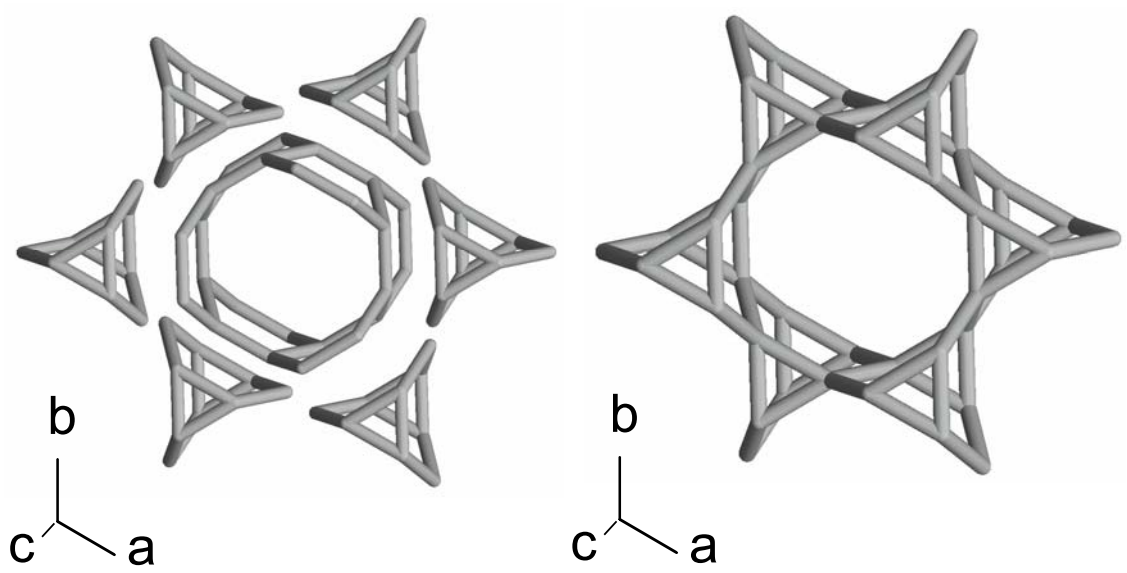


Fig. NPO.1.1. The framework structure of NPO-type compounds in the highest possible topological symmetry *P* $6_3/m\ m\ c$. View parallel [001] rotated by 10° about [100] and 15° about [120].



a Linkage of *bb44* units forming the *kok* unit. **b** The complete assemblage shown in a) (enlarged).

Fig. NPO.1.2. Building scheme of the NPO-type framework. View parallel [001] rotated by 10° about [210] and [010].

P 6_3/*m m c*	NPO-I.	Highest possible topological symmetry.
t3		
c, 2**a**+**b**, **b**		
A m a m	NPO-III.	Intermediate step to describe the transformation.
t2		
a, **b**, **c**		
A m a 2	NPOP-VI.	Intermediate step to describe the transformation.
k2		
a, **b**, **c**		
½, ¼, 0		Origin shift to conform to the IT and NPO2003a01 settings.
P n a 2_1	NPO-XII.	Space group of the oxonitridophosphate.

Fig. NPO.1.3 The Bärnighausen tree illustrating the symmetry relationship of the NPO types.

Table NPO.1.1 Atomic site relationships of the NPO types.

NPO-I *P* $6_3/m\,m\,c$	NPO-III *A m a m*	NPO-VI *A m a* 2	NPO-XII *P n a* 2_1
T1 [6(h), *m m* 2]	T11 [8(g), *m* . .]	T11a [4(b), *m* . .]	T11a [4(a), 1]
		T11b [4(b), *m* . .]	T11b [4(a), 1]
	T12 [4(c), *m* 2 *m*]	T12 [4(b), *m* . .]	T12 [4(a), 1]
O1 [6(h), *m m* 2]	O11 [8(g), *m* . .]	O11a [4(b), *m* . .]	O11a [4(a), 1]
		O11b [4(b), *m* . .]	O11b [4(a), 1]
	O12 [4(c), *m* 2 *m*]	O12 [4(b), *m* . .]	O12 [4(a), 1]
O2 [6(g), . 2/*m* .]	O21 [8(d), $\bar{1}$]	O21 [8(c), 1]	O21a [4(a), 1]
			O21b [4(a), 1]
	O22 [4(b), . . 2/*m*]	O22 [4(a), . . 2]	O22 [4(a), 1]

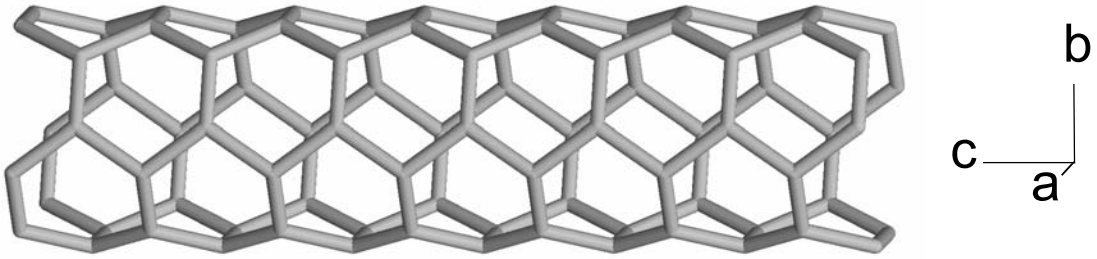


Fig. NPO.1.4. The 12-ring channel formed by *kok* units parallel [001]. View parallel [100] rotated by 10° about [120] and [010].

NPO.2 Compounds and crystal data

Table NPO.2.1 Chemical data.

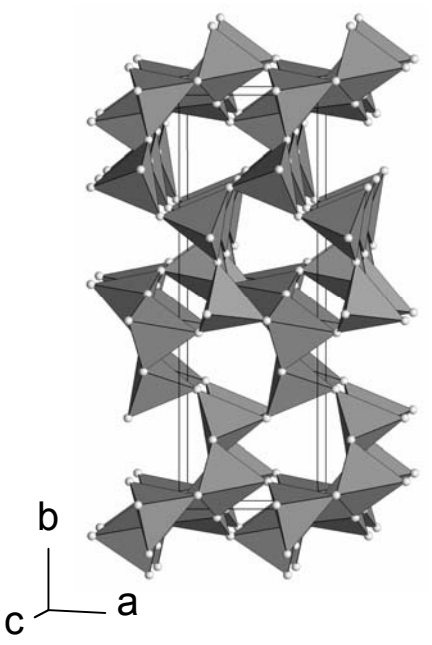
FD = framework density CE = cation exchange TT = thermal treatment REF=reference
SM = source of material SR = sorbate T = temperature of thermal treatment [K]

code	chemical composition	FD	SM	CE	SR	TT	T	REF
NPO-XII *P n a* 2_1								
NPO2003a01	$Li_8H_{4.5}\cdot P_{12}O_2N_{22}\cdot Cl_{2.5}$	21.7	S	-	Cl	-	-	2003Cor1
NPO2004a01	$Li_8H_{4.5}\cdot P_{12}O_2N_{22}\cdot Cl_{2.5}$	21.7	S	-	Cl	-	-	2004Cor1
NPO2004a02	$Li_8H_{4.5}\cdot P_{12}O_2N_{22}\cdot (Cl,Br)_{2.5}$	21.4	S	-	Cl	-	-	2004Cor1

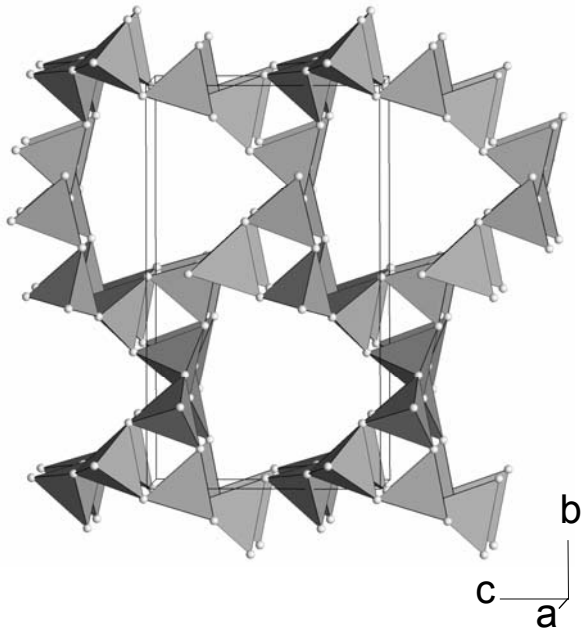
Table NPO.2.2 Structural parameters of the NPO-type compound.

code	*a* [Å]	*b* [Å]	*c* [Å]	*V* [Å^3]	*T* [K]	reference
NPO-XII *P n a* 2_1						
NPO2003a01	4.753(1)	14.208(3)	8.203(2)	554	n.s.	2003Cor1
NPO2004a01	4.753(1)	14.208(3)	8.203(2)	554	n.s.	2004Cor1
NPO2004a02	4.766(1)	14.263(3)	8.235(2)	560	n.s.	2004Cor1

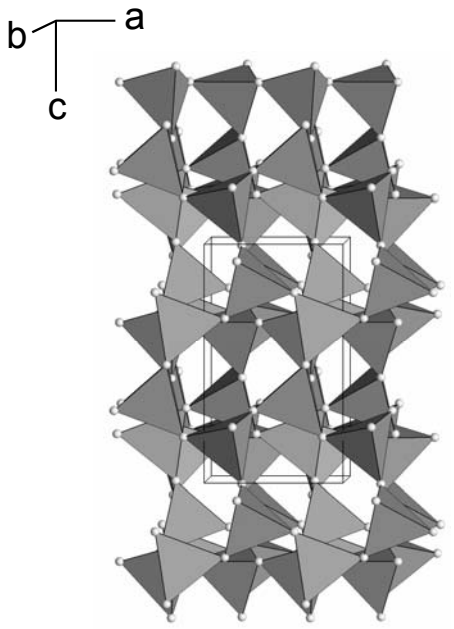
NPO.3 Framework structure of NPO-XII compound ($Pna2_1$, IT #33)



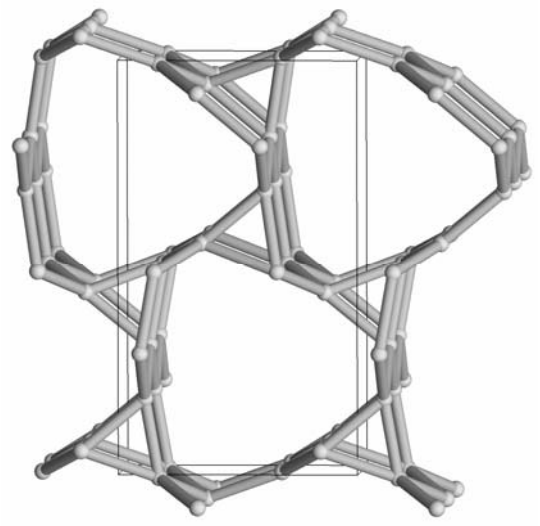
a View parallel **c** rotated by 2° about **a** and **b**.



b View parallel **a** rotated by 4° about **b** and **c**.



c View parallel **b** rotated by 1° about **a** and **c**.



d Ball and stick model corresponding to b).

Fig. NPO.3.1 Projections of the NPO-XII crystal structure of oxonitridophosphate, $Li_8H_{4.5} \cdot P_{12}O_2N_{22} \cdot Cl_{2.5}$ (NPO2003a01, 2003Cor1).

Table NPO.3.1 Atomic coordinates and site definitions for oxonitridophosphate, $Li_8H_{4.5} \cdot P_{12}O_2N_{22} \cdot Cl_{2.5}$ (NPO2003a01, 2003Cor1).

atom	*x*	*y*	*z*	B_{eq} [Å^2]	site symmetry	Wyckoff position	no. of atoms in unit cell
P11a	0.6766(2)	0.93573(6)	0.6421(1)	0.9106(2)	1	4(a)	4
P11b	0.8251(2)	0.00329(6)	0.3226(1)	0.8922(2)	1	4(a)	4
P12	0.7917(1)	0.30923(8)	0.8770(1)	1.0106(2)	1	4(a)	4
(N,O)11a	0.7930(7)	0.8971(3)	0.2631(5)	1.0633(8)	1	4(a)	3.67/0.33
(N,O)11b	0.7558(4)	0.8325(4)	0.5672(6)	1.013(1)	1	4(a)	3.67/0.33
(N,O)12	0.7703(5)	0.5199(4)	0.0041(7)	1.282(1)	1	4(a)	3.67/0.33
(N,O)21a	0.6515(5)	0.0708(2)	0.1987(4)	1.1133(5)	1	4(a)	3.67/0.33
(N,O)21b	0.6500(5)	0.4602(2)	0.3077(4)	0.9949(5)	1	4(a)	3.67/0.33
(N,O)22	0.6184(4)	0.2153(2)	0.8323(4)	0.9712(5)	1	4(a)	3.67/0.33
Cl1	0.989(2)	0.2510(2)	0.441(1)	12.501(2)	1	4(a)	2.56(3)
Li1	0.833(3)	0.145(1)	0.623(2)	0.033(3)	1	4(a)	2.16(2)
Li2	0.181(3)	0.602(1)	0.008(2)	0.033(4)	1	4(a)	2.0(1)
Li3	0.862(3)	0.203(1)	0.200(2)	0.033(4)	1	4(a)	1.7(1)

Table NPO.3.2 Selected interatomic distances and angles for oxonitridophosphate, $Li_8H_{4.5} \cdot P_{12}O_2N_{22} \cdot Cl_{2.5}$ (NPO2003a01, 2003Cor1).

	T - O [Å]	T - O - T [°]		T - O [Å]	T - O - T [°]
P11a - (N,O)21b	1.627(3)	127.5(2)	P11b - (N,O)12	1.574(6)	125.4(4)
P11a - (N,O)21a	1.630(3)	129.1(2)	P11b - (N,O)11a	1.593(4)	125.5(3)
P11a - (N,O)11b	1.634(6)	121.1(3)	P11b - (N,O)21a	1.623(3)	129.1(2)
P11a - (N,O)12	1.666(6)	125.4(4)	P11b - (N,O)21b	1.634(3)	127.5(2)
mean	1.639	125.8	mean	1.606	126.9
P12 - (N,O)11a	1.610(4)	125.5(3)			
P12 - (N,O)22	1.611(3)	127.7(2)			
P12 - (N,O)11b	1.611(5)	121.1(3)			
P12 - (N,O)22	1.633(2)	127.7(2)			
mean	1.616	125.5			

NPO.4 Chemical composition

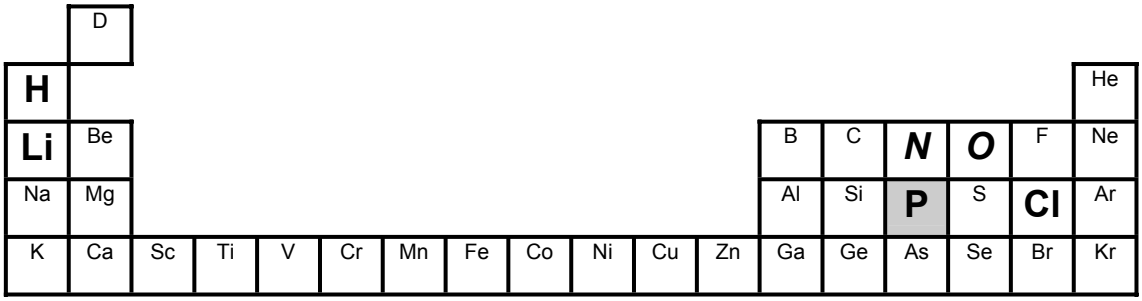


Fig. NPO.4.1 Chemical elements (highlighted) occurring in the NPO-type compound. Framework cations are in grey fields.

NPO.5 Flexibility and apertures

There is insufficient information available about the NPO-type to judge its flexibility.

The openings of the 12-rings in the framework of NPO-type are distorted into a triangular shape with the largest free diameters of slightly over 3 Å and almost 4.5 Å. In the FAU-type the openings measure close to 7.5 Å.

NPO.6 Other information

Catalytic properties have not been reported for NPO-type compounds.

NPO.7 References

2001Bae1 Baerlocher, C., Meier, W.M., Olson, D.H.: Atlas of Zeolite Framework Types, 5th Ed., Amsterdam: Elsevier, 2001.

2003Cor1 Correll, S., Oeckler, O., Stock, N., Schnick, W.: Angew. Chem. Int. Ed. **42** (2003) 3549.

2004Cor1 Correll, S., Stock, N., Oeckler, O., Senker, J., Nilges, T., Schnick, W.: Z. anorg. allgem. Chem. **630** (2004) 2205.

2004Cor2 Correll, S., Oeckler, O., Stock, N., Schnick, W.: Silicates Industr. **69** (2004) 19.

Gone to press March 1, 2006