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Supertetrahedral Anions in the Phosphidosilicates $Na_{1.25}Ba_{0.875}Si_3P_5$ and $Na_{31}Ba_5Si_{52}P_{83}$

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Abstract: Solid ionic conductors are one key component of all-solid-state batteries, and recent studies with lithium, sodium and potassium phosphidosilicates revealed remarkable ion conduction capabilities in these compounds. We report the synthesis and crystal structures of two quaternary phosphidosilicates with sodium and barium, which crystallize in new structures types. $Na_{1.25}Ba_{0.875}Si_3P_5$ contains layers of T3 supertetrahedra, while $Na_{31}Ba_5Si_{52}P_{83}$ forms defect T5 entities and contains Si-Si bonds and P_3 trimers. Though T_1-relaxometry data indicate a relatively low activation energy for Na^+ migration of 0.16 eV, the crystal structures lack sufficient three-dimensional migration paths necessary for fast sodium ion conductivity.

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Table S1. Fractional atomic coordinates, equivalent displacement parameters (Å^2) and occupancy factors of $Na_{1.25}Ba_{0.875}Si_3P_5$.

atom	Wyckoff	x	y	z	U_{eq}	Occ. (<1)
Ba1	8*f*	0.000000	0.20847 (2)	0.08780 (4)	0.01843 (16)	0.4052 (19)
Ba2	4*c*	0.000000	0.41347 (2)	0.250000	0.0391 (2)	0.808 (3)
Ba3	4*c*	0.000000	0.79762 (2)	0.250000	0.01851 (9)	
Na1	8*f*	0.000000	0.20847 (2)	0.08780 (4)	0.01843 (16)	0.595 (2)
Na2	8*e*	0.2456 (5)	0.000000	0.000000	0.0399 (8)	0.823 (5)
Na3	4*c*	0.000000	0.41347 (2)	0.250000	0.0391 (2)	0.192 (3)
Na4	4*c*	0.000000	0.91409 (13)	0.250000	0.0478 (15)	0.733 (11)
Si1	16*h*	0.25116 (9)	0.10945 (2)	0.08484 (6)	0.01093 (13)	
Si2	8*f*	0.000000	0.32129 (3)	0.07770 (9)	0.01184 (18)	
Si3	4*c*	0.000000	0.03358 (4)	0.250000	0.0114 (2)	
Si4	4*c*	0.000000	0.53264 (4)	0.250000	0.0116 (2)	
Si5	4*c*	0.000000	0.68381 (4)	0.250000	0.0118 (2)	
P1	16*h*	0.26239 (9)	0.35654 (2)	0.08266 (6)	0.01537 (14)	
P2	8*g*	0.23757 (13)	0.14767 (3)	0.250000	0.01199 (16)	
P3	8*g*	0.25204 (13)	0.49366 (3)	0.250000	0.01388 (17)	
P4	8*f*	0.000000	0.06891 (3)	0.07724 (8)	0.01158 (16)	
P5	8*f*	0.000000	0.27958 (3)	0.58292 (9)	0.0243 (2)	
P6	8*f*	0.000000	0.56828 (3)	0.07749 (8)	0.01209 (17)	
P7	4*c*	0.000000	0.28421 (4)	0.250000	0.0148 (2)	

Table S2. Atomic displacement parameters (Å^2) of $Na_{1.25}Ba_{0.875}Si_3P_5$.

atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0253 (3)	0.0157 (2)	0.0143 (2)	0.000	0.000	0.00122 (15)
Ba2	0.0799 (5)	0.0163 (2)	0.0211 (2)	0.000	0.000	0.000
Ba3	0.02080 (16)	0.01630 (15)	0.01843 (16)	0.000	0.000	0.000
Na1	0.0253 (3)	0.0157 (2)	0.0143 (2)	0.000	0.000	0.00122 (15)
Na2	0.070 (2)	0.0303 (12)	0.0192 (11)	0.000	0.000	−0.0053 (9)
Na3	0.0799 (5)	0.0163 (2)	0.0211 (2)	0.000	0.000	0.000
Na4	0.048 (3)	0.030 (2)	0.066 (3)	0.000	0.000	0.000
Si1	0.0089 (3)	0.0139 (3)	0.0100 (3)	−0.0006 (2)	−0.0002 (2)	0.0011 (2)
Si2	0.0118 (4)	0.0136 (4)	0.0101 (4)	0.000	0.000	0.0010 (3)
Si3	0.0089 (5)	0.0128 (6)	0.0127 (6)	0.000	0.000	0.000
Si4	0.0098 (6)	0.0126 (6)	0.0125 (6)	0.000	0.000	0.000
Si5	0.0116 (6)	0.0135 (6)	0.0103 (6)	0.000	0.000	0.000
P1	0.0111 (3)	0.0220 (3)	0.0131 (3)	−0.0019 (2)	−0.0018 (2)	0.0060 (2)
P2	0.0097 (4)	0.0154 (4)	0.0108 (4)	−0.0001 (3)	0.000	0.000

P3	0.0095 (4)	0.0130 (4)	0.0191 (4)	−0.0003 (3)	0.000	0.000
P4	0.0094 (4)	0.0130 (4)	0.0124 (4)	0.000	0.000	0.0005 (3)
P5	0.0485 (7)	0.0136 (4)	0.0109 (4)	0.000	0.000	−0.0003 (3)
P6	0.0100 (4)	0.0140 (4)	0.0123 (4)	0.000	0.000	0.0003 (3)
P7	0.0212 (6)	0.0145 (6)	0.0086 (5)	0.000	0.000	0.000

Table S3. Selected bond distances in $Na_{1.25}Ba_{0.875}Si_3P_5$ in Å.

atoms	distance	atoms	distance	atoms	distance	atoms	distance
Ba1—P5^{i}	3.0749 (11)	Ba2—Na4^{ix}	3.5840 (1)	Na2—P4^{xx}	3.057 (2)	Si1—P4	2.2707 (9)
Ba1—P7	3.1458 (12)	Ba2—Na4^{x}	3.5840 (1)	Na2—P6^{ix}	3.078 (2)	Si2—P1	2.2323 (9)
Ba1—P2	3.2290 (9)	Ba2—Si2^{i}	3.6762 (11)	Na2—P6^{iv}	3.078 (2)	Si2—P1^{viii}	2.2324 (9)
Ba1—P2^{ii}	3.2290 (9)	Ba2—Si2	3.6764 (11)	Na2—Si3^{xx}	3.4777 (17)	Si2—P5^{i}	2.2785 (14)
Ba1—P1^{iii}	3.3735 (8)	Ba2—P6^{xi}	3.6844 (9)	Na2—Si3	3.4777 (17)	Si2—P7	2.2904 (12)
Ba1—P1^{iv}	3.3735 (8)	Ba2—P6^{vii}	3.6844 (9)	Na2—Si4^{ix}	3.4995 (18)	Si3—P3^{x}	2.2382 (12)
Ba1—Ba1^{i}	3.5971 (9)	Ba3—P5^{xii}	3.2174 (11)	Na2—Si4i^{v}	3.4995 (18)	Si3—P3^{xix}	2.2382 (12)
Ba1—P5^{v}	3.6074 (2)	Ba3—P5^{xiii}	3.2174 (11)	Na2—Na2^{xx}	3.521 (7)	Si3—P4	2.2626 (12)
Ba1—P5^{vi}	3.6074 (2)	Ba3—P1^{xiv}	3.2210 (7)	Na2—Na2^{xxi}	3.646 (7)	Si3—P4^{i}	2.2627 (12)
Ba1—Ba3^{vii}	3.7517 (5)	Ba3—P1^{xv}	3.2210 (7)	Na4—P1^{xvii}	3.192 (3)	Si4—P3	2.2424 (12)
Ba1—Si1	3.8241 (8)	Ba3—P1^{xvi}	3.2210 (7)	Na4—P1^{xvi}	3.192 (3)	Si4—P3^{ii}	2.2425 (12)
Ba1—Si1^{viii}	3.8242 (8)	Ba3—P1^{xvii}	3.2210 (7)	Na4—P1^{xiv}	3.192 (3)	Si4—P6	2.2658 (12)
Ba2—P3^{ii}	3.2754 (10)	Ba3—P7^{xvii}	3.6129 (2)	Na4—P1^{xv}	3.192 (3)	Si4—P6^{i}	2.2658 (12)
Ba2—P3	3.2755 (10)	Ba3—P7^{xviii}	3.6129 (2)	Na4—P3^{xiv}	3.242 (4)	Si5—P5^{xiii}	2.2336 (13)
Ba2—P1^{viii}	3.2775 (8)	Ba3—Na4	3.968 (5)	Na4—P3^{xvii}	3.242 (4)	Si5—P5^{xii}	2.2336 (13)
Ba2—P1^{ii}	3.2775 (8)	Na2—P3^{xix}	2.7807 (1)	Si1—P1^{iv}	2.1913 (9)	Si5—P2^{xvii}	2.2483 (12)
Ba2—P1^{i}	3.2775 (8)	Na2—P3^{iv}	2.7807 (1)	Si1—P2	2.2492 (8)	Si5—P2^{xiv}	2.2483 (12)
Ba2—P1	3.2776 (8)	Na2—P4	3.057 (2)	Si1—P6^{ix}	2.2707 (9)	Si1—P4	2.2707 (9)

Symmetry codes: (i) x, *y*, −*z*+1/2; (ii) −*x*, *y*, −*z*+1/2; (iii) *x*−1/2, −*y*+1/2, −*z*; (iv) −*x*+1/2, −*y*+1/2, −*z*; (v) −*x*+1/2, −*y*+1/2, *z*−1/2; (vi) −*x*−1/2, −*y*+1/2, *z*−1/2; (vii) −*x*, −*y*+1, −*z*; (viii) −*x*, *y*, *z*; (ix) *x*+1/2, *y*−1/2, *z*; (x) *x*−1/2, *y*−1/2, *z*; (xi) −*x*, −*y*+1, *z*+1/2; (xii) −*x*, −*y*+1, *z*−1/2; (xiii) −*x*, −*y*+1, −*z*+1; (xiv) −*x*+1/2, *y*+1/2, −*z*+1/2; (xv) *x*−1/2, *y*+1/2, −*z*+1/2; (xvi) −*x*+1/2, *y*+1/2, *z*; (xvii) *x*−1/2, *y*+1/2, *z*; (xviii) *x*+1/2, *y*+1/2, *z*; (xix) −*x*+1/2, *y*−1/2, −*z*+1/2; (xx) −*x*, −*y*, −*z*; (xxi) −*x*+1, −*y*, −*z*; (xxii) −*x*, −*y*, *z*+1/2; (xxiii) −*x*+1/2, −*y*+1/2, *z*+1/2; (xxiv) −*x*−1/2, −*y*+1/2, *z*+1/2.

Table S4. Fractional atomic coordinates, equivalent displacement parameters (Å^2) and occupancy factors of $Na_{31}Ba_5Si_{52}P_{83}$.

atom	Wyckoff	x	y	z	U_{eq}	Occ. (<1)
Ba1	8*f*	0.03838(3)	0.28816(2)	0.44990(3)	0.03319(13)	0.5
Ba2	8*f*	0.42512(2)	0.12558(2)	0.29605(2)	0.02363(6)	
Ba3	8*f*	0.43398(2)	0.00233(2)	0.06545(2)	0.03283(7)	
Na1	8*f*	0.00223(14)	0.10926(17)	0.49733(14)	0.1048(16)	
Na2	8*f*	0.00686(11)	0.16477(9)	0.36852(12)	0.0533(6)	

Na3	8*f*	0.0430(3)	0.30328(17)	0.4023(4)	0.083 (2)	0.5
Na4	8*f*	0.0624(7)	0.3881(3)	0.2299(5)	0.135(5)	0.5
Na5	8*f*	0.0636(3)	0.4140 (3)	0.2057 (4)	0.082 (2)	0.5
Na6	8*f*	0.0721 (4)	0.2081 (2)	0.5718 (3)	0.0715 (18)	0.5
Na7	8*f*	0.0875 (2)	0.44421 (11)	0.11510 (16)	0.0598 (13)	0.743 (8)
Na8	8*f*	0.24210 (12)	0.39581 (6)	0.19832 (9)	0.0392 (5)	
Na9	8*f*	0.24662 (15)	0.33869 (11)	0.32971 (16)	0.0814 (11)	
Na10	8*f*	0.2477 (2)	0.44216 (9)	0.04221 (14)	0.0820 (10)	
Na11	8*f*	0.2522 (3)	0.2775 (2)	0.4487 (4)	0.224 (4)	
Na12	8*f*	0.25708 (15)	0.30915 (7)	0.00968 (9)	0.0502 (6)	
Na13	8*f*	0.3839 (2)	0.39190 (13)	0.1225 (2)	0.110 (2)	0.892 (10)
Na14	8*f*	0.40704 (13)	0.14171 (8)	0.07478 (9)	0.0459 (5)	
Na15	8*f*	0.41501 (15)	0.34166 (8)	0.29286 (11)	0.0545 (6)	
Na16	8*f*	0.43369 (13)	0.25448 (7)	0.09847 (8)	0.0443 (5)	
Na17	8*f*	0.4914 (2)	0.4690 (2)	0.1078 (2)	0.130 (3)	0.878 (10)
Na18	4*e*	0.000000	0.0063 (2)	0.250000	0.096 (2)	0.972 (15)
Na19	4*e*	0.000000	0.23869 (13)	0.250000	0.0637 (11)	
Si1	8*f*	0.12797 (5)	0.35015 (3)	0.06876 (4)	0.01613 (19)	
Si2	8*f*	0.14325 (6)	0.23599 (3)	0.06283 (4)	0.01532 (19)	
Si3	8*f*	0.14759 (5)	0.29167 (3)	0.19249 (4)	0.01338 (17)	
Si4	8*f*	0.15704 (5)	0.12513 (3)	0.05375 (4)	0.01428 (18)	
Si5	8*f*	0.16056 (5)	0.01184 (3)	0.04449 (4)	0.01362 (18)	
Si6	8*f*	0.16119 (5)	0.06083 (3)	0.17363 (4)	0.01297 (17)	
Si7	8*f*	0.16278 (5)	0.10598 (3)	0.54268 (4)	0.01372 (18)	
Si8	8*f*	0.16296 (5)	0.17611 (3)	0.18630 (4)	0.01279 (17)	
Si9	8*f*	0.16315 (5)	0.04632 (3)	0.41873 (4)	0.01474 (18)	
Si10	8*f*	0.16454 (5)	0.22990 (3)	0.31329 (4)	0.01346 (18)	
Si11	8*f*	0.16732 (5)	0.11122 (3)	0.30336 (4)	0.01368 (18)	
Si12	8*f*	0.16750 (5)	0.16597 (3)	0.42771 (4)	0.01435 (18)	
Si13	8*f*	0.18625 (5)	0.45145 (3)	0.36336 (4)	0.01375 (18)	
Si14	8*f*	0.29282 (5)	0.30290 (3)	0.15019 (4)	0.01311 (17)	
Si15	8*f*	0.30819 (5)	0.18534 (3)	0.15002 (4)	0.01325 (17)	
Si16	8*f*	0.31110 (5)	0.06675 (3)	0.14294 (4)	0.01319 (17)	
Si17	8*f*	0.31122 (5)	0.00422 (3)	0.26096 (4)	0.01410 (18)	
Si18	8*f*	0.31121 (5)	0.23848 (3)	0.27591 (4)	0.01215 (17)	
Si19	8*f*	0.31647 (5)	0.05175 (3)	0.39075 (4)	0.01445 (18)	
Si20	8*f*	0.32087 (5)	0.10468 (3)	0.51419 (4)	0.01544 (18)	
Si21	8*f*	0.32141 (5)	0.16746 (3)	0.39691 (4)	0.01361 (18)	
Si22	8*f*	0.33889 (5)	0.49532 (3)	0.20764 (4)	0.01324 (17)	

Si23	8*f*	0.34165 (5)	0.44621 (3)	0.33394 (4)	0.01315 (17)
Si24	8*f*	0.44033 (5)	0.24940 (3)	0.23187 (4)	0.01304 (17)
Si25	8*f*	0.44218 (5)	0.00773 (3)	0.22698 (4)	0.01398 (18)
Si26	8*f*	0.53629 (6)	0.10431 (4)	0.01670 (5)	0.0208 (2)
P1	8*f*	0.06627 (5)	0.39356 (4)	0.44006 (4)	0.0225 (2)
P2	8*f*	0.07249 (6)	0.54290 (4)	0.06602 (5)	0.0279 (2)
P3	8*f*	0.07437 (5)	0.44766 (3)	0.32417 (4)	0.01828 (18)
P4	8*f*	0.07790 (5)	0.40785 (3)	0.01360 (4)	0.01930 (19)
P5	8*f*	0.09242 (5)	0.29268 (3)	0.00918 (4)	0.01777 (18)
P6	8*f*	0.09491 (5)	0.34891 (3)	0.14242 (4)	0.01832 (18)
P7	8*f*	0.10536 (5)	0.23290 (3)	0.13459 (4)	0.01500 (17)
P8	8*f*	0.10650 (6)	0.18167 (3)	0.00068 (4)	0.0220 (2)
P9	8*f*	0.11451 (5)	0.00588 (3)	0.11124 (4)	0.01454 (17)
P10	8*f*	0.11484 (5)	0.12101 (3)	0.12364 (4)	0.01305 (16)
P11	8*f*	0.11639 (5)	0.04637 (3)	0.48593 (4)	0.01397 (16)
P12	8*f*	0.11657 (5)	0.05668 (3)	0.24087 (4)	0.01412 (16)
P13	8*f*	0.11874 (5)	0.17174 (3)	0.25340 (4)	0.01327 (16)
P14	8*f*	0.11905 (5)	0.29095 (3)	0.26748 (4)	0.01677 (18)
P15	8*f*	0.12014 (5)	0.10811 (3)	0.36871 (4)	0.01485 (17)
P16	8*f*	0.12105 (5)	0.11210 (3)	0.61046 (4)	0.01588 (17)
P17	8*f*	0.12370 (5)	0.16694 (3)	0.49356 (4)	0.01713 (18)
P18	8*f*	0.12431 (5)	0.22756 (3)	0.38152 (4)	0.01681 (18)
P19	8*f*	0.22142 (5)	0.39077 (3)	0.41677 (4)	0.01363 (16)
P20	8*f*	0.22370 (5)	0.49260 (3)	0.16714 (4)	0.01396 (16)
P21	8*f*	0.22584 (5)	0.44311 (3)	0.29334 (4)	0.01382 (16)
P22	8*f*	0.24177 (5)	0.36008 (3)	0.09607 (4)	0.01576 (17)
P23	8*f*	0.25854 (5)	0.24264 (3)	0.09306 (4)	0.01516 (17)
P24	8*f*	0.26254 (5)	0.29965 (3)	0.22710 (4)	0.01323 (16)
P25	8*f*	0.27277 (5)	0.12761 (3)	0.08910 (4)	0.01386 (16)
P26	8*f*	0.27463 (5)	0.06746 (3)	0.21473 (4)	0.01354 (16)
P27	8*f*	0.27620 (5)	0.01137 (3)	0.07962 (4)	0.01393 (16)
P28	8*f*	0.27732 (5)	0.17644 (3)	0.22442 (4)	0.01289 (16)
P29	8*f*	0.27839 (5)	0.04335 (3)	0.46111 (4)	0.01609 (17)
P30	8*f*	0.28076 (5)	0.23274 (3)	0.35208 (4)	0.01360 (16)
P31	8*f*	0.28253 (5)	0.11168 (3)	0.33466 (4)	0.01478 (17)
P32	8*f*	0.28390 (5)	0.16936 (3)	0.46901 (4)	0.01530 (17)
P33	8*f*	0.37585 (6)	0.48831 (3)	0.13755 (4)	0.01998 (19)
P34	8*f*	0.37902 (5)	0.42929 (3)	0.00814 (4)	0.01809 (18)
P35	8*f*	0.38405 (5)	0.43940 (3)	0.26701 (4)	0.01661 (17)

P36	8*f*	0.40505 (5)	0.31098 (3)	0.18038 (4)	0.01743 (18)	
P37	8*f*	0.42026 (5)	0.18631 (3)	0.18168 (4)	0.01638 (17)	
P38	8*f*	0.42198 (5)	0.01163 (4)	0.30508 (4)	0.0211 (2)	
P39	8*f*	0.42275 (5)	0.24213 (3)	0.31297 (4)	0.01698 (18)	
P40	8*f*	0.42381 (5)	0.06940 (3)	0.17732 (4)	0.01710 (18)	
P41	8*f*	0.56460 (5)	0.16504 (4)	0.07307 (4)	0.0209 (2)	
P42	8*f*	0.01904 (15)	0.28372 (9)	0.51020 (13)	0.0397 (6)	0.5

Table S5. Atomic displacement parameters (Å^2) of $Na_{31}Ba_5Si_{52}P_{83}$.

atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.0237(3)	0.0350(3)	0.0402(3)	-0.0194(2)	0.0120(2)	-0.0034(2)
Ba2	0.02674(12)	0.02313(11)	0.02034(11)	-0.00194(9)	0.00866(9)	0.00406(9)
Ba3	0.04358(16)	0.03085(14)	0.02699(13)	0.00248(10)	0.01716(12)	-0.01025(12)
Na1	0.0256(13)	0.215(5)	0.0616(19)	0.040(2)	0.0052(12)	-0.0109(19)
Na2	0.0267(11)	0.0564(15)	0.0757(18)	0.0158(13)	0.0191(11)	0.0037(10)
Na3	0.044(3)	0.033(3)	0.143(6)	-0.037(3)	0.008(3)	0.013(2)
Na4	0.253(14)	0.088(6)	0.120(8)	-0.025(6)	0.134(9)	0.029(8)
Na5	0.053(3)	0.074(5)	0.125(7)	-0.057(5)	0.040(4)	0.001(3)
Na6	0.103(5)	0.074(4)	0.062(3)	0.015(3)	0.059(4)	0.035(4)
Na7	0.068(3)	0.045(2)	0.056(2)	-0.0191(16)	0.0137(18)	0.0057(17)
Na8	0.0652(14)	0.0238(9)	0.0351(10)	-0.0108(8)	0.0268(10)	-0.0058(9)
Na9	0.0657(18)	0.085(2)	0.109(3)	-0.074(2)	0.0513(18)	-0.0390(16)
Na10	0.135(3)	0.0385(14)	0.076(2)	0.0078(14)	0.047(2)	-0.0253(17)
Na11	0.106(4)	0.241(7)	0.362(10)	-0.255(8)	0.129(5)	-0.090(4)
Na12	0.109(2)	0.0258(10)	0.0343(11)	0.0027(8)	0.0480(13)	0.0058(11)
Na13	0.067(3)	0.062(2)	0.181(5)	0.066(3)	0.029(3)	0.0077(18)
Na14	0.0687(16)	0.0470(13)	0.0329(11)	0.0021(9)	0.0319(11)	0.0095(11)
Na15	0.0839(19)	0.0336(11)	0.0441(13)	-0.0131(10)	0.0237(13)	0.0032(12)
Na16	0.0727(16)	0.0352(11)	0.0205(9)	-0.0003(8)	0.0138(10)	0.0047(10)
Na17	0.046(2)	0.237(7)	0.111(4)	-0.058(4)	0.037(2)	-0.031(3)
Na18	0.037(2)	0.155(6)	0.084(4)	0.000	0.011(2)	0.000
Na19	0.0260(16)	0.056(2)	0.105(3)	0.000	0.0208(19)	0.000
Si1	0.0208(19)	0.0145(4)	0.0148(4)	0.0043(3)	0.0037(4)	0.0006(4)
Si2	0.0228(5)	0.0103(4)	0.0115(4)	0.0012(3)	0.0053(4)	0.0012(4)
Si3	0.0159(4)	0.0115(4)	0.0137(4)	0.0013(3)	0.0070(4)	0.0010(3)
Si4	0.0203(5)	0.0105(4)	0.0123(4)	0.0003(3)	0.0068(4)	-0.0001(3)
Si5	0.0176(5)	0.0116(4)	0.0117(4)	-0.0004(3)	0.0059(4)	0.0008(3)
Si6	0.0168(4)	0.0118(4)	0.0110(4)	-0.0002(3)	0.0064(4)	0.0002(3)

Si7	0.0173(5)	0.0138(4)	0.0112(4)	0.0008(3)	0.0068(4)	-0.0010(3)
Si8	0.0163(4)	0.0113(4)	0.0117(4)	0.0000(3)	0.0065(4)	-0.0006(3)
Si9	0.0215(5)	0.0127(4)	0.0116(4)	-0.0008(3)	0.0083(4)	-0.0023(4)
Si10	0.0168(4)	0.0127(4)	0.0131(4)	0.0004(3)	0.0083(4)	-0.0001(3)
Si11	0.0194(5)	0.0116(4)	0.0109(4)	0.0002(3)	0.0068(4)	0.0000(3)
Si12	0.0192(5)	0.0133(4)	0.0123(4)	0.0007(3)	0.0082(4)	-0.0007(4)
Si13	0.0170(4)	0.0130(4)	0.0121(4)	0.0006(3)	0.0067(4)	0.0002(3)
Si14	0.0161(4)	0.0108(4)	0.0129(4)	0.0012(3)	0.0063(4)	0.0015(3)
Si15	0.0178(5)	0.0107(4)	0.0134(4)	-0.0006(3)	0.0084(4)	-0.0008(3)
Si16	0.0170(4)	0.0115(4)	0.0117(4)	0.0005(3)	0.0065(4)	0.0002(3)
Si17	0.0155(4)	0.0132(4)	0.0131(4)	-0.0001(3)	0.0051(4)	-0.0006(3)
Si18	0.0143(4)	0.0119(4)	0.0117(4)	0.0001(3)	0.0067(3)	-0.0003(3)
Si19	0.0183(5)	0.0128(4)	0.0120(4)	-0.0019(3)	0.0058(4)	-0.0019(3)
Si20	0.0184(5)	0.0168(4)	0.0130(4)	0.0005(3)	0.0082(4)	-0.0008(4)
Si21	0.0158(4)	0.0130(4)	0.0124(4)	0.0008(3)	0.0061(4)	-0.0005(3)
Si22	0.0174(4)	0.0121(4)	0.0109(4)	0.0009(3)	0.0063(4)	0.0012(3)
Si23	0.0166(4)	0.0121(4)	0.0114(4)	0.0011(3)	0.0063(4)	0.0010(3)
Si24	0.0147(4)	0.0114(4)	0.0151(4)	0.0003(3)	0.0082(4)	0.0004(3)
Si25	0.0163(4)	0.0131(4)	0.0115(4)	0.0006(3)	0.0044(4)	-0.0002(3)
Si26	0.0170(5)	0.0225(5)	0.0209(5)	0.0072(4)	0.0055(4)	0.0035(4)
P1	0.0206(5)	0.0272(5)	0.0191(5)	-0.0008(4)	0.0072(4)	-0.0039(4)
P2	0.0181(5)	0.0269(5)	0.0313(6)	0.0105(4)	0.0019(4)	0.0008(4)
P3	0.0168(4)	0.0168(4)	0.0196(4)	0.0011(3)	0.0056(4)	0.0002(3)
P4	0.0162(4)	0.0161(4)	0.0239(5)	0.0091(4)	0.0061(4)	0.0030(3)
P5	0.0233(5)	0.0156(4)	0.0120(4)	0.0015(3)	0.0046(4)	0.0019(4)
P6	0.0222(5)	0.0156(4)	0.0186(4)	0.0041(3)	0.0096(4)	0.0060(4)
P7	0.0189(4)	0.0123(4)	0.0130(4)	0.0011(3)	0.0055(3)	-0.0008(3)
P8	0.0379(6)	0.0111(4)	0.0122(4)	0.0004(3)	0.0050(4)	0.0008(4)
P9	0.0193(4)	0.0124(4)	0.0125(4)	-0.0003(3)	0.0070(3)	0.0004(3)
P10	0.0167(4)	0.0111(4)	0.0111(4)	0.0003(3)	0.0052(3)	0.0004(3)
P11	0.0180(4)	0.0129(4)	0.0115(4)	0.0008(3)	0.0064(3)	-0.0009(3)
P12	0.0186(4)	0.0128(4)	0.0123(4)	-0.0006(3)	0.0076(3)	-0.0004(3)
P13	0.0171(4)	0.0118(4)	0.0120(4)	0.0003(3)	0.0069(3)	0.0001(3)
P14	0.0218(5)	0.0145(4)	0.0170(4)	0.0014(3)	0.0109(4)	0.0027(3)
P15	0.0195(4)	0.0140(4)	0.0127(4)	0.0001(3)	0.0081(3)	-0.0005(3)
P16	0.0219(5)	0.0145(4)	0.0129(4)	0.0029(3)	0.0088(4)	0.0043(3)
P17	0.0230(5)	0.0169(4)	0.0146(4)	0.0028(3)	0.0108(4)	0.0017(4)
P18	0.0237(5)	0.0144(4)	0.0170(4)	0.0019(3)	0.0131(4)	0.0020(3)
P19	0.0171(4)	0.0130(4)	0.0115(4)	-0.0002(3)	0.0065(3)	-0.0007(3)

P20	0.0178(4)	0.0117(4)	0.0121(4)	0.0010(3)	0.0056(3)	0.0009(3)
P21	0.0170(4)	0.0130(4)	0.0121(4)	0.0002(3)	0.0064(3)	0.0007(3)
P22	0.0184(4)	0.0122(4)	0.0181(4)	0.0040(3)	0.0087(4)	0.0026(3)
P23	0.0230(5)	0.0112(4)	0.0134(4)	0.0003(3)	0.0095(4)	-0.0005(3)
P24	0.0160(4)	0.0112(4)	0.0135(4)	0.0005(3)	0.0070(3)	0.0005(3)
P25	0.0195(4)	0.0110(4)	0.0123(4)	0.0002(3)	0.0076(3)	0.0000(3)
P26	0.0172(4)	0.0125(4)	0.0119(4)	-0.0005(3)	0.0068(3)	-0.0001(3)
P27	0.0183(4)	0.0120(4)	0.0124(4)	-0.0006(3)	0.0071(3)	0.0001(3)
P28	0.0158(4)	0.0114(4)	0.0125(4)	0.0001(3)	0.0069(3)	-0.0002(3)
P29	0.0222(5)	0.0150(4)	0.0120(4)	0.0003(3)	0.0077(4)	-0.0002(3)
P30	0.0169(4)	0.0132(4)	0.0128(4)	0.0004(3)	0.0082(3)	-0.0001(3)
P31	0.0203(4)	0.0130(4)	0.0122(4)	-0.0002(3)	0.0077(3)	-0.0004(3)
P32	0.0198(4)	0.0146(4)	0.0133(4)	-0.0004(3)	0.0086(3)	-0.0016(3)
P33	0.0310(5)	0.0171(4)	0.0174(4)	0.0053(3)	0.0156(4)	0.0086(4)
P34	0.0265(5)	0.0118(4)	0.0126(4)	-0.0004(3)	0.0044(4)	0.0013(3)
P35	0.0227(5)	0.0143(4)	0.0160(4)	0.0035(3)	0.0109(4)	0.0047(3)
P36	0.0187(4)	0.0133(4)	0.0221(5)	0.0038(3)	0.0101(4)	0.0010(3)
P37	0.0177(4)	0.0134(4)	0.0202(4)	-0.0028(3)	0.0098(4)	-0.0001(3)
P38	0.0174(4)	0.0298(5)	0.0156(4)	0.0018(4)	0.0062(4)	-0.0011(4)
P39	0.0145(4)	0.0234(5)	0.0142(4)	0.0022(3)	0.0069(3)	0.0002(3)
P40	0.0169(4)	0.0152(4)	0.0183(4)	0.0026(3)	0.0061(4)	-0.0004(3)
P41	0.0192(5)	0.0285(5)	0.0153(4)	0.0008(4)	0.0071(4)	0.0080(4)
P42	0.0367(14)	0.0346(13)	0.0413(15)	-0.0076(11)	0.0087(12)	0.0005(11)

Table S6. Selected bond distances in $Na_{31}Ba_5Si_{52}P_{83}$ in Å.

atoms	distance	atoms	distance	atoms	distance	atoms	distance
Ba1—Na3	1.331 (9)	Na5—P6	2.802 (6)	Na14—P4^{vii}	2.828 (2)	Si9—P33^{vi}	2.2232 (14)
Ba1—P42	1.738 (3)	Na5—P3^{ii}	2.912 (6)	Na14—P5^{vii}	2.931 (2)	Si9—P29	2.2518 (15)
Ba1—P41^{i}	3.2732 (12)	Na5—P38^{ix}	3.035 (9)	Na14—P37	2.945 (2)	Si9—P15	2.2604 (14)
Ba1—P1	3.3141 (13)	Na5—P3	3.093 (8)	Na14—P25	3.050 (3)	Si9—P11	2.2879 (13)
Ba1—P5^{ii}	3.3367 (12)	Na5—Si25^{ix}	3.370 (6)	Na14—P40	3.324 (2)	Si10—P14	2.2120 (14)
Ba1—P7^{ii}	3.4030 (11)	Na5—P21	3.395 (7)	Na14—Si1^{vii}	3.416 (2)	Si10—P18	2.2142 (13)
Ba1—P6^{ii}	3.4190 (12)	Na5—Na8	3.916 (7)	Na14—P41	3.444 (3)	Si10—P30	2.2687 (14)
Ba1—P18	3.5097 (11)	Na5—Na5^{ii}	4.144 (16)	Na14—Na16	3.518 (3)	Si10—P13	2.2919 (13)
Ba1—Si26^{i}	3.7149 (12)	Na6—P42	2.771 (7)	Na15—P36	2.926 (3)	Si11—P13	2.2521 (13)
Ba1—P32^{iii}	3.7435 (11)	Na6—P17	2.908 (5)	Na15—P35	3.083 (3)	Si11—P15	2.2537 (13)
Ba1—Na6	3.781 (6)	Na6—P16	3.147 (6)	Na15—P39	3.088 (3)	Si11—P31	2.2548 (14)
Ba1—Na2	4.233 (3)	Na6—P39^{iii}	3.257 (6)	Na15—P16^{iii}	3.177 (3)	Si11—P12	2.2597 (13)

Ba2—P28	3.3255 (9)	Na6—Na16^{i}	3.468 (6)	Na15—P24	3.262 (3)	Si12—P17	2.2111 (13)
Ba2—P37	3.4105 (10)	Na6—Na15^{iii}	3.662 (6)	Na15—Si24	3.369 (2)	Si12—P18	2.2190 (14)
Ba2—P41^{iv}	3.4525 (10)	Na6—Na9^{iii}	3.935 (7)	Na16—P5v^{ii}	2.937 (2)	Si12—P32	2.2735 (14)
Ba2—P40	3.4557 (10)	Na6—Na11^{iii}	3.997 (8)	Na16—P36	2.947 (2)	Si12—P15	2.2795 (14)
Ba2—P40^{iv}	3.4672 (10)	Na7—P4	2.734 (4)	Na16—P39^{iv}	3.006 (3)	Si13—P3	2.1858 (14)
Ba2—P38	3.5049 (12)	Na7—P38^{ix}	2.954 (3)	Na16—P8^{vii}	3.026 (2)	Si13—P19	2.2465 (13)
Ba2—P26	3.5224 (10)	Na7—P6	2.994 (4)	Na16—P37	3.062 (2)	Si13—P21	2.2604 (13)
Ba2—P31	3.5639 (10)	Na7—P20	3.048 (4)	Na16—Si24	3.328 (2)	Si13—P27^{ix}	2.2761 (13)
Ba2—P39	3.6035 (11)	Na7—P2	3.239 (4)	Na17—P9^{x}	2.821 (5)	Si14—P36	2.2112 (14)
Ba2—P37^{iv}	3.6230 (10)	Na7—Si1	3.354 (3)	Na17—P33	2.906 (4)	Si14—P22	2.2243 (13)
Ba2—Na14^{iv}	3.792 (3)	Na7—P1^{ii}	3.379 (4)	Na17—P34	2.958 (5)	Si14—P23	2.2802 (13)
Ba2—Ba2^{iv}	4.6383 (5)	Na7—Na8	3.455 (4)	Na17—Si23^{iv}	3.331 (5)	Si14—P24	2.2843 (13)
Ba3—P2^{v}	3.1927 (12)	Na8—P22	2.809 (2)	Na17—P35^{iv}	3.346 (6)	Si15—P37	2.1913 (14)
Ba3—P3^{vi}	3.3247 (11)	Na8—P21	2.946 (2)	Na17—Na18^{x}	3.715 (5)	Si15—P28	2.2454 (13)
Ba3—P1^{vi}	3.3394 (12)	Na8—P24	3.028 (2)	Na18—P12	3.007 (4)	Si15—P23	2.2519 (13)
Ba3—P4^{vii}	3.3551 (10)	Na8—P20	3.057 (2)	Na18—P12^{ii}	3.007 (4)	Si15—P25	2.2708 (13)
Ba3—Na7^{v}	3.485 (4)	Na8—P35	3.121 (2)	Na18—P33^{xi}	3.0645 (17)	Si16—P40	2.2016 (14)
Ba3—P38^{iv}	3.4937 (11)	Na8—P6	3.216 (3)	Na18—P33^{vi}	3.0645 (17)	Si16—P26	2.2434 (13)
Ba3—P27	3.5256 (10)	Na8—Si14	3.438 (2)	Na18—Si22^{xi}	3.1744 (13)	Si16—P27	2.2489 (13)
Ba3—P2^{vii}	3.5583 (14)	Na8—Si1	3.502 (2)	Na18—Si22^{vi}	3.1744 (13)	Si16—P25	2.2630 (13)
Ba3—P40	3.5769 (10)	Na8—Na9	3.727 (5)	Na18—P35^{xi}	3.366 (4)	Si17—P38	2.1797 (14)
Ba3—P29^{viii}	3.5948 (10)	Na8—Na15	3.872 (4)	Na18—P35^{vi}	3.366 (4)	Si17—P26	2.2389 (13)
Ba3—Na10^{vii}	4.106 (4)	Na9—P14	2.929 (3)	Na19—P14^{ii}	2.878 (2)	Si17—P20^{vi}	2.2524 (13)
Ba3—Na14	4.332 (2)	Na9—P19	2.940 (3)	Na19—P14	2.878 (2)	Si17—P21^{vi}	2.2718 (13)
Na1—P16	2.971 (3)	Na9—P24	3.000 (3)	Na19—Si10	3.2275 (11)	Si18—P39	2.1785 (14)
Na1—P34^{i}	2.986 (3)	Na9—P16^{iii}	3.016 (3)	Na19—Si10^{ii}	3.2275 (11)	Si18—P28	2.2564 (13)
Na1—P10^{ii}	3.103 (3)	Na9—P21	3.313 (4)	Na19—P13	3.229 (3)	Si18—P24	2.2581 (13)
Na1—Si7	3.140 (3)	Na9—P30	3.329 (4)	Na19—P13^{ii}	3.230 (3)	Si18—P30	2.2732 (13)
Na1—Si4^{ii}	3.145 (3)	Na9—Si7^{iii}	3.474 (3)	Na19—P18^{ii}	3.3432 (11)	Si19—P2^{vi}	2.1884 (15)
Na1—P17	3.164 (4)	Na9—Na11	3.515 (11)	Na19—P18	3.3432 (11)	Si19—P29	2.2467 (13)
Na1—P11	3.203 (4)	Na9—Na15	4.046 (4)	Si1—P6	2.2410 (14)	Si19—P31	2.2584 (13)
Na1—P8^{ii}	3.221 (5)	Na10—P22	2.890 (3)	Si1—P4	2.2431 (14)	Si19—P20^{vi}	2.2741 (13)
Na1—Na6	3.567 (9)	Na10—P29^{ix}	3.148 (3)	Si1—P5	2.2461 (14)	Si20—P1^{iii}	2.2112 (15)
Na1—Na2	3.715 (4)	Na10—P33	3.165 (4)	Si1—P22	2.2572 (14)	Si20—P19^{iii}	2.2673 (13)
Na1—Na17^{i}	3.761 (6)	Na10—Na13	3.195 (5)	Si2—P5	2.2062 (14)	Si20—P32	2.2684 (14)
Na2—P15	2.969 (3)	Na10—P27^{vii}	3.249 (3)	Si2—P8	2.2100 (14)	Si20—P29	2.2790 (14)
Na2—P10^{ii}	2.992 (2)	Na10—P34	3.260 (4)	Si2—P7	2.2647 (14)	Si21—P41^{iv}	2.2344 (14)
Na2—P18	3.066 (3)	Na10—Na12	4.183 (4)	Si2—P23	2.2681 (15)	Si21—P31	2.2488 (13)
Na2—Si12	3.137 (2)	Na11—P32^{iii}	2.978 (5)	Si3—P6	2.1937 (13)	Si21—P32	2.2660 (13)

Na2—P7^{ii}	3.150 (3)	Na11—P17^{iii}	2.989 (4)	Si3—P14	2.2126 (13)	Si21—P30	2.2941 (13)
Na2—P17	3.151 (3)	Na11—P18	2.992 (4)	Si3—P24	2.2578 (14)	Si22—P33	2.2197 (13)
Na2—P13^{ii}	3.184 (3)	Na11—P30	3.070 (5)	Si3—P7	2.2705 (13)	Si22—P35	2.2300 (13)
Na2—Si8^{ii}	3.331 (2)	Na11—Na11^{iii}	3.124 (19)	Si4—P8	2.1947 (14)	Si22—P20	2.2489 (14)
Na2—Na19	3.718 (4)	Na11—P32	3.380 (8)	Si4—P34^{vii}	2.2074 (13)	Si22—P12^{ix}	2.2704 (13)
Na3—P1	2.907 (5)	Na11—Si12^{iii}	3.384 (5)	Si4—P25	2.2605 (14)	Si23—P16^{iii}	2.2180 (13)
Na3—P6^{ii}	3.032 (5)	Na11—Si10	3.503 (6)	Si4—P10	2.2849 (13)	Si23—P35	2.2247 (13)
Na3—P42	3.032 (10)	Na12—P22	2.811 (2)	Si5—P34^{vii}	2.2024 (13)	Si23—P9i^{x}	2.2612 (13)
Na3—P18	3.064 (5)	Na12—P23	2.927 (2)	Si5—P27	2.2575 (14)	Si23—P21	2.2614 (14)
Na3—Na19	4.102 (7)	Na12—P23^{vii}	2.952 (2)	Si5—P11^{viii}	2.2713 (13)	Si24—P39	2.2405 (13)
Na3—Na4^{ii}	4.124 (13)	Na12—P25^{vii}	3.026 (2)	Si5—P9	2.2738 (13)	Si24—P36	2.2475 (13)
Na3—Na11	4.202 (7)	Na12—P8^{vii}	3.029 (3)	Si6—P26	2.2234 (14)	Si24—P37	2.2603 (13)
Na4—Na5	1.009 (11)	Na12—Si14	3.334 (2)	Si6—P10	2.2331 (13)	Si24—Si24^{iv}	2.330 (2)
Na4—P6	2.837 (7)	Na12—Si4^{vii}	3.510 (2)	Si6—P9	2.2522 (13)	Si25—P38	2.1882 (14)
Na4—P3	2.936 (8)	Na12—Na14^{vii}	3.616 (4)	Si6—P12	2.2595 (13)	Si25—P3^{vi}	2.1986 (14)
Na4—Na4^{ii}	3.20 (2)	Na12—Na12^{vii}	3.658 (4)	Si7—P17	2.2159 (14)	Si25—P40	2.2182 (13)
Na4—P14	3.212 (11)	Na12—Na16	3.904 (4)	Si7—P16	2.2327 (13)	Si25—Si25^{iv}	2.263 (2)
Na4—P3^{ii}	3.241 (12)	Na12—Na13	3.967 (6)	Si7—P19^{iii}	2.2615 (14)	Si26—P2v	2.2215 (15)
Na4—Na7	3.597 (11)	Na13—P36	2.826 (4)	Si7—P11	2.2914 (13)	Si26—P4^{vii}	2.2675 (15)
Na4—Na5^{ii}	3.735 (12)	Na13—P22	2.988 (4)	Si8—P7	2.2294 (13)	Si26—P1^{xii}	2.2727 (16)
Na4—Na9	4.017 (14)	Na13—P33	2.995 (4)	Si8—P28	2.2308 (14)	Si26—P41	2.2768 (16)
Na4—Na8	4.212 (12)	Na13—P34	3.078 (5)	Si8—P13	2.2505 (13)	P5—P42^{ii}	2.238 (3)
Na5—Na7	2.706 (11)	Na13—Na17	3.412 (7)	Si8—P10	2.2643 (13)	P41—P42^{xii}	2.171 (3)

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

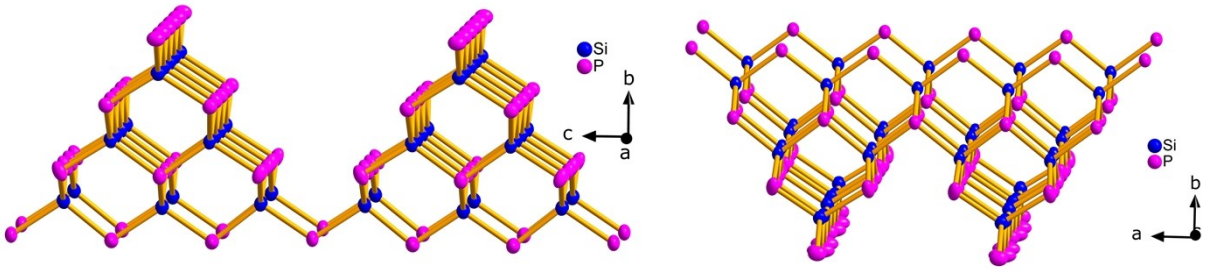

Figure S1. Ball-stick models of T3 supertetrahedra in $Na_{1.25}Ba_{0.875}Si_3P_5$ along the crystallographic *a*- and *c*-axis showing their connectivity by a common vertex (left) and by a common SiP_4 tetrahedron (right). Ellipsoids are drawn with 90 % probability.

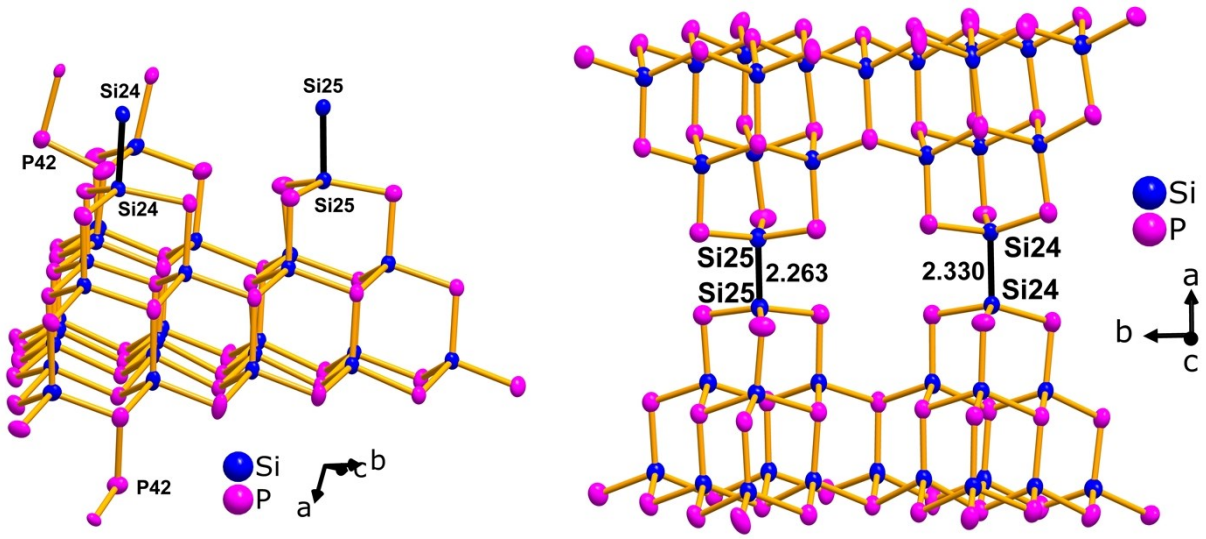

Figure S2. Ball-stick models of T3 supertetrahedra in $Na_{31}Ba_5Si_{52}P_{83}$ showing their connectivity by common SiP_4 tetrahedra to defect T5 supertetrahedra (left) and the condensation to a three dimensional anionic network by homonuclear silicon bonds (right). Ellipsoids are drawn with 90 % probability and the homonuclear silicon bonds are depicted in black.

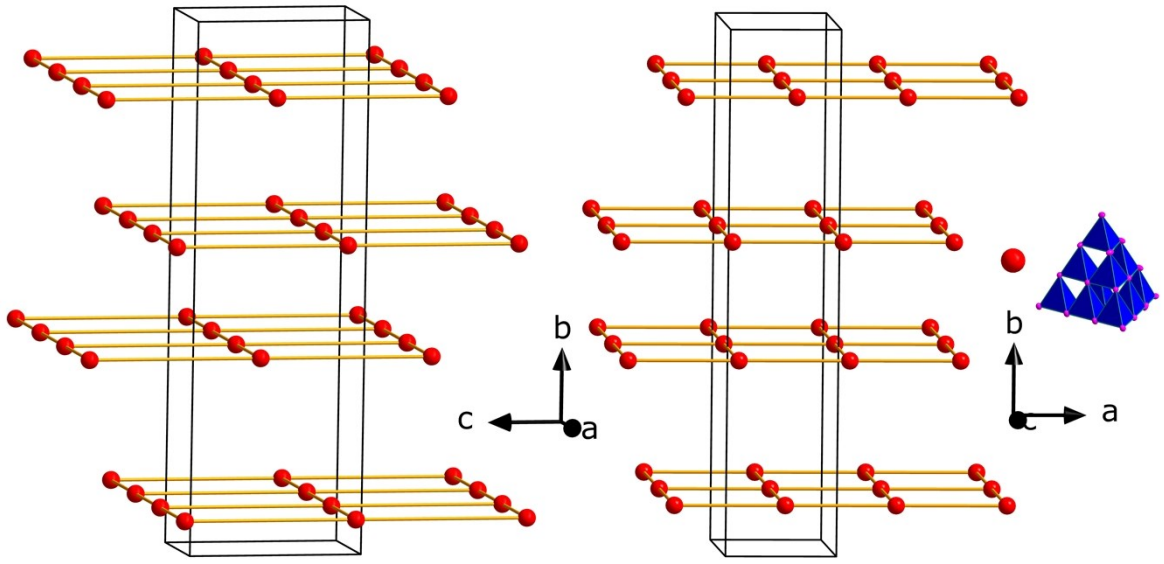

Figure S3. Topology of the anionic sheets in $Na_{1.25}Ba_{0.875}Si_3P_5$, which can be assigned to distorted sql-nets. Every red position corresponds to a T3 supertetrahedron. The distortion arises from different condensations of the T3 supertetrahedra either by common vertices or by fusion.

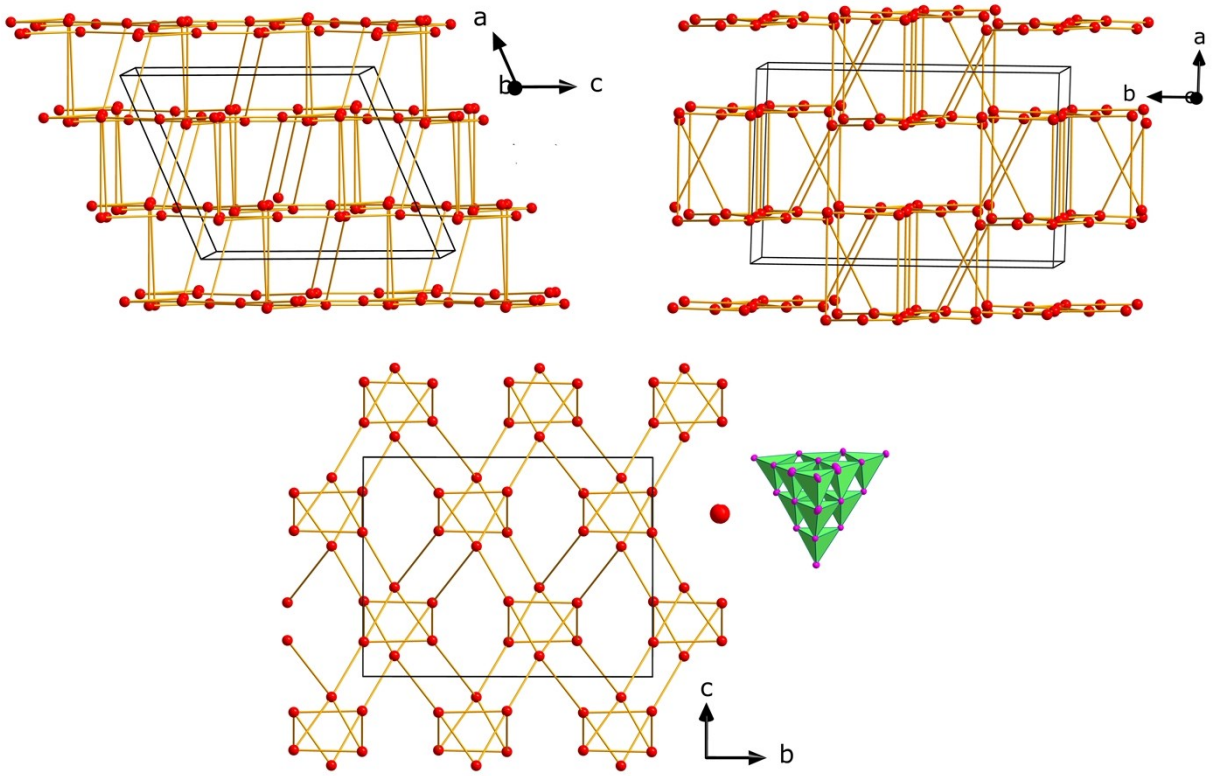

Figure S4. Topology of the anionic 26-nodal network (TD10 = 596) in $Na_{31}Ba_5Si_{52}P_{83}$ in *b* (left), *c* (right) and *a* (bottom) direction. Every red position corresponds to a T3 supertetrahedron either with a SiP_4 or a SiP_3Si vertex.

The preparation of polycristalline samples was conducted in an argon filled glovebox due to the high sensitivity towards air and moisture of the compounds. Respective samples were ground and filled in silica capillaries with a diameter of 0.2 mm and subsequently sealed. The according powder X-ray diffractograms were obtained by using the setup described in the publication for this Supporting Information and the fundamental parameter approach. Based on the structure models of the single-crystal X-ray structure determination and refinement the according powder diffraction patterns were fitted. Therefore, the unit cell parameters were refined as well as the atom positions of barium, silicon and phosphorus with no significant changes. The occupancies derived from the single-crystal refinement were not refined and the peak shapes and background were fitted using pseudo-Voigt and shifted Chebyshev, respectively. For the $Na_{31}Ba_5Si_{52}P_{83}$ samples the difference curve revealed a side phase beside unreacted silicon (1.4 %), which we were able to refine with the single-crystal structure model of $Na_{23}Si_{37}P_{57}$ (9.8 %). The according results are compiled in Table S5.

Table S7. Crystallographic data of powder Rietveld refinements of $Na_{1.25}Ba_{0.875}Si_3P_5$ and $Na_{31}Ba_5Si_{52}P_{83}$.

Formula	$Na_{1.25}Ba_{0.875}Si_3P_5$	$Na_{31}Ba_5Si_{52}P_{83}$
Space group	*Cmcm* (No. 63)	*C*2/*c* (No. 15)
a / Å	7.1682(2)	21.279(1)
b / Å	34.158(2)	30.688(2)
c / Å	11.0886(3)	25.341(1)
β / °	90	113.559(5)
V_{cell} / Å³	2715.1(2)	15168(2)
$\rho_{X\text{-}ray}$ / g·cm^{-1}	2.733(5)	2.3751(2)
Diffractometer	Stoe Stadi P	
Radiation	Mo-Kα1 (λ = 0.709319 Å)	
Detector	Mythen 1K	
Monochromator	Ge(111)	
2Θ - range / °	2.000 – 55.940	1.000 - 57.145
Data points	3597	3744
Background function	Shifted Chebyshev	
Refined parameters (background parameters)	48 (18)	234 (20)
GooF	3.302	3.019
R_p; R_{wp}	0.040; 0.053	0.033; 0.044
R_{exp}; R_{Bragg}	0.016; 0.027	0.014; 0.012

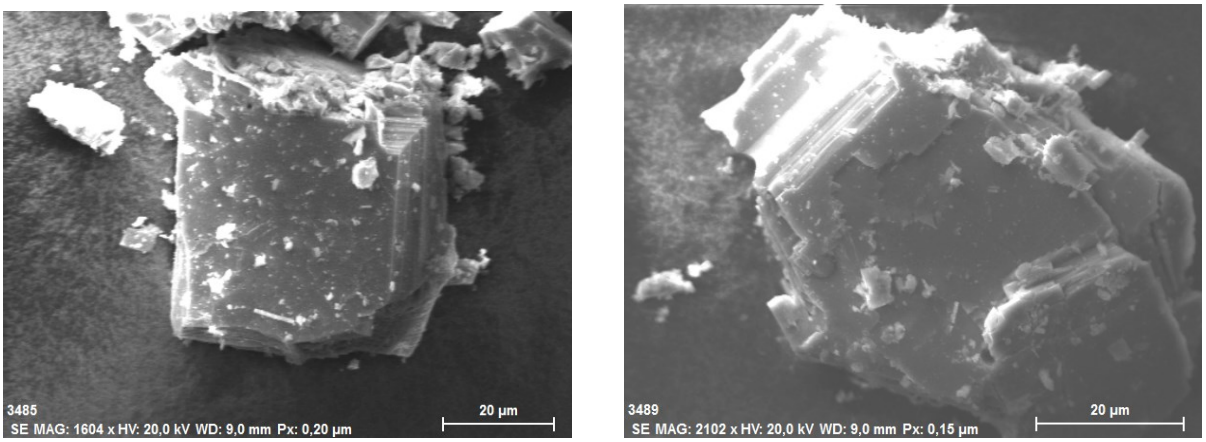

Figure S5. Representative scanning electron microscopic photographs of $Na_{1.25}Ba_{0.875}Si_3P_5$.

Table S8. Elemental analysis by EDX of $Na_{1.25}Ba_{0.875}Si_3P_5$, signals of oxygen were not taken into account due to hydrolysis.

	Na	Ba	Si	P
EDX point 1 / atom-%	13.09	8.35	26.52	52.04
EDX point 2 / atom-%	12.49	9.28	26.48	51.75
EDX point 3 / atom-%	12.85	9.73	26.42	51.00
EDX point 4 / atom-%	12.51	9.45	26.49	51.55
EDX point 5 / atom-%	12.26	8.28	26.78	52.68
EDX point 6 / atom-%	12.55	8.08	26.96	52.41
EDX point 7 / atom-%	12.15	9.14	26.86	51.85
EDX point 8 / atom-%	12.38	9.48	26.65	51.48
EDX point 9 / atom-%	12.25	9.28	26.79	51.68
EDX point 10 / atom-%	12.28	8.65	26.81	52.27
EDX point 11 / atom-%	11.47	8.78	27.04	52.70
EDX point 12 / atom-%	12.05	8.01	27.18	52.76
EDX point 13 / atom-%	10.11	8.73	28.91	52.24
EDX point 14 / atom-%	13.08	9.18	26.49	51.25
EDX point 15 / atom-%	12.24	9.53	26.23	52.00
Average / atom-%	12.25	8.93	26.84	51.98
Calculated / atom-%	12.4	8.6	29.6	49.4

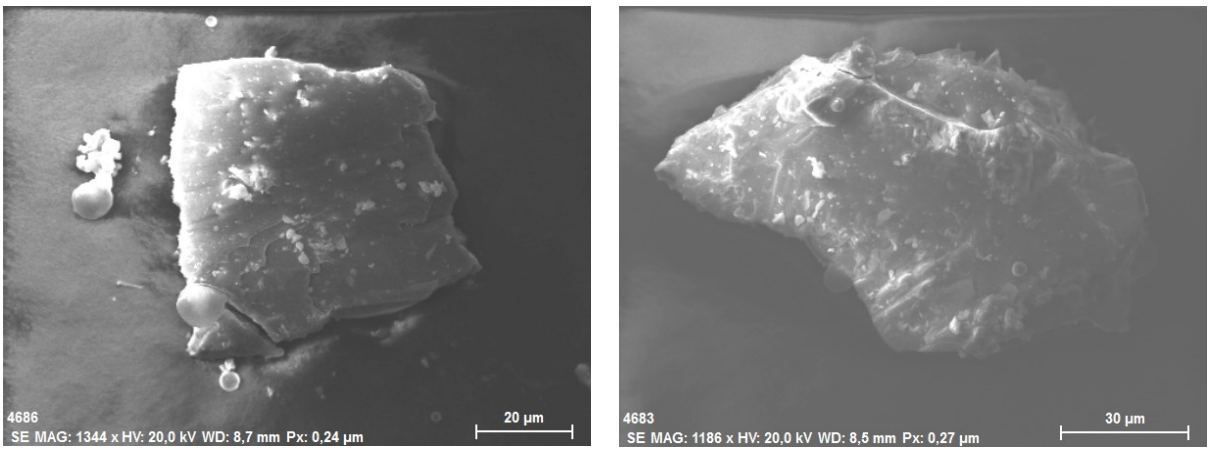

Figure S6. Representative scanning electron microscopic photographs of $Na_{31}Ba_5Si_{52}P_{83}$.

Table S9. Elemental analysis by EDX of $Na_{31}Ba_5Si_{52}P_{83}$, signals of oxygen were not taken into account due to hydrolysis.

	Na	Ba	Si	P
EDX point 1 / atom-%	17.27	3.56	27.54	51.64
EDX point 2 / atom-%	18.81	3.54	26.51	51.14
EDX point 3 / atom-%	18.69	3.42	26.09	51.80
EDX point 4 / atom-%	18.35	3.76	26.79	51.10
EDX point 5 / atom-%	18.21	2.85	26.42	52.52
EDX point 6 / atom-%	19.48	3.81	26.03	50.69
EDX point 7 / atom-%	17.92	3.41	26.87	51.80
EDX point 8 / atom-%	18.22	3.15	26.29	52.34
EDX point 9 / atom-%	15.64	3.24	28.65	52.47
EDX point 10 / atom-%	17.99	3.45	26.59	51.97
EDX point 11 / atom-%	17.51	3.28	27.71	51.51
EDX point 12 / atom-%	17.62	3.61	28.83	49.94
EDX point 13 / atom-%	15.56	3.52	29.52	51.40
EDX point 14 / atom-%	20.53	3.30	24.25	51.92
EDX point 15 / atom-%	18.44	3.24	27.02	51.31
Average / atom-%	18.0	3.4	27.0	51.6
Calculated / atom-%	18.13	2.92	30.41	48.54

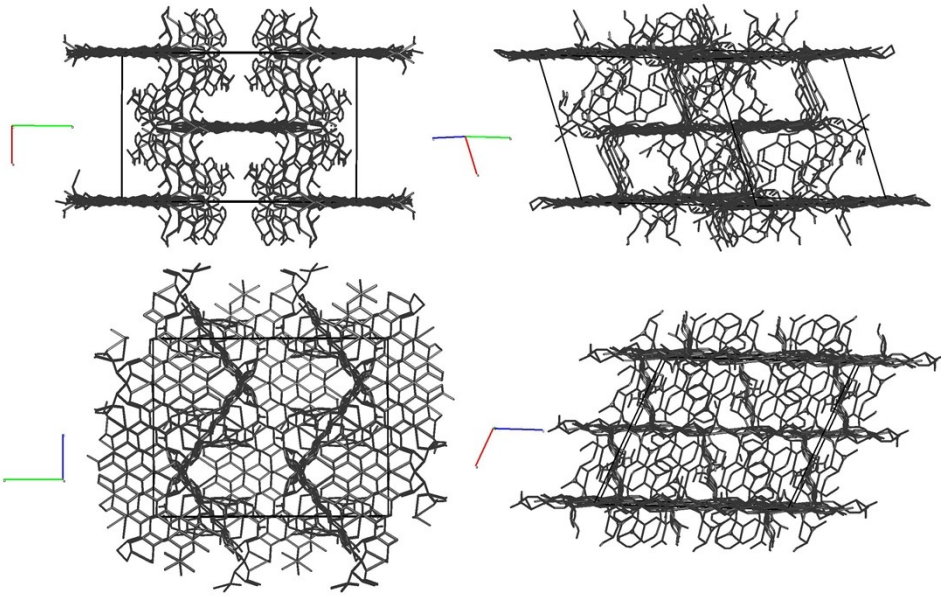

Figure S7. Geometrically calculated possible sodium migration paths for $Na_{31}Ba_5Si_{52}P_{83}$. Wide channels along *c* are formed which are connected by narrow and short passages along the T3 faces assuming predominantly one-dimensional sodium ion conduction.

To obtain the ^{23}Na-NMR spin-lattice relaxation time (T_1) at different temperatures, the saturation recovery technique was used. For an estimate of the activation energies, the characteristic correlation times τ_c of the dynamic processes causing the spin relaxation are assumed to follow an Arrhenius type of behavior with activation energy E_A:

$$\tau_c = \tau_0 \exp\left(\frac{E_A}{k_B T}\right)$$

In the so-called low-temperature regime ($\omega_0\tau_c >> 1$), the relaxation rate $1/T_1$ for a single dynamic process is given by the following form, which can be linearized and fitted to extract the activation energy:

$$R_1 = \frac{1}{T_1} = \frac{4}{3} G(0) \frac{1}{\omega_0^2 \tau_0} \exp\left(-\frac{E_A}{k_B T}\right)$$

For a single dynamic process, the integrated signal intensities are expected to follow a mono-exponential function. As may be seen from Figure S8 (left), using a mono-exponential does not lead to a good fit for $Na_{31}Ba_5Si_{52}P_{83}$. In contrast, a bi-exponential fit describes the data much better, see Figure S8 (right). The existence of a second exponential function implies the presence of at least one more dynamic process on a much slower time scale. From the M_0 values returned by the bi-exponential fit it may be seen that slow process constitutes the minority component of the signal by a factor of about one quarter. Therefore, this process could be due to sodium ions in the side phase or related to non-mobile or slow moving sodium in the target structure.

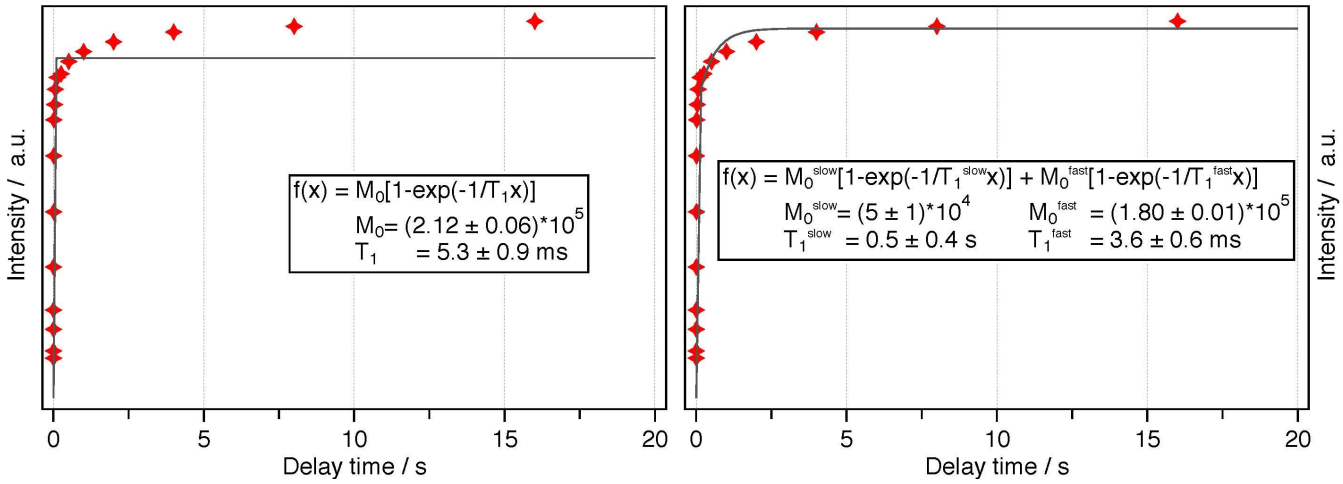

Figure S8. ^{23}Na-NMR spin-lattice relaxation time (T_1) data for $Na_{31}Ba_5Si_{52}P_{83}$ at 274K. The integrated signal intensities were fitted with either a mono-exponential (left) or bi-exponential (right) function.