Supplementary information

Minimal liquid-assisted method for synthesis of ammonium, sodium, and potassium intercalated zirconium hydrogen phosphate: The effect of the cation used on the formation of an α- or γ-structure

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Table S1. Molar ratios P/Zr and M/Zr, and formulas for samples prepared from γ-zirconium phosphate using ion exchange

M	P/Zr	M/Zr	H2O [wt%]	Formula
NH_4	2.04 ± 0.08	4.66*	0	$NH_4Zr(PO_4)(HPO_4)$
Na	2.10 ± 0.09	1.01 ± 0.03	7.8	$NaHZr(PO_4)(HPO_4)\cdot 1.4H_2O$
K	1.94 ± 0.08	0.98 ± 0.10	0	$KZr(PO_4)(HPO_4)$

* Nitrogen content in wt% in the intercalate determined by organic elemental analysis. The theoretical nitrogen content for the composition γ-$NH_4Zr(PO_4)(HPO_4)$ is 4.67 wt%.

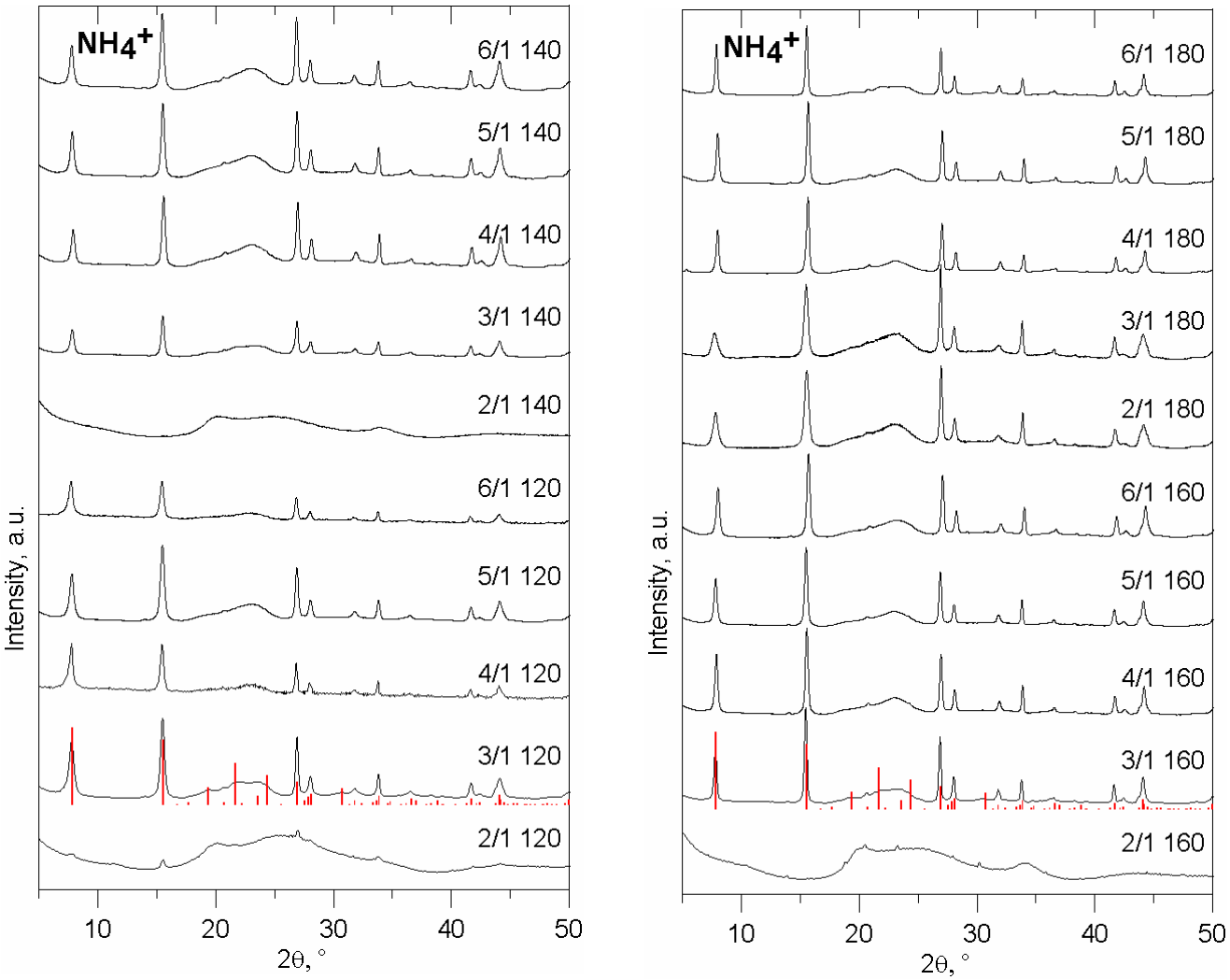

Figure S1. Powder X-ray diffraction patterns of ammonium intercalates prepared at various P/Zr ratios and temperatures. Red lines correspond to γ-$H(NH_4)Zr(PO_4)_2$ (JCPDS No. 00-033-0842).

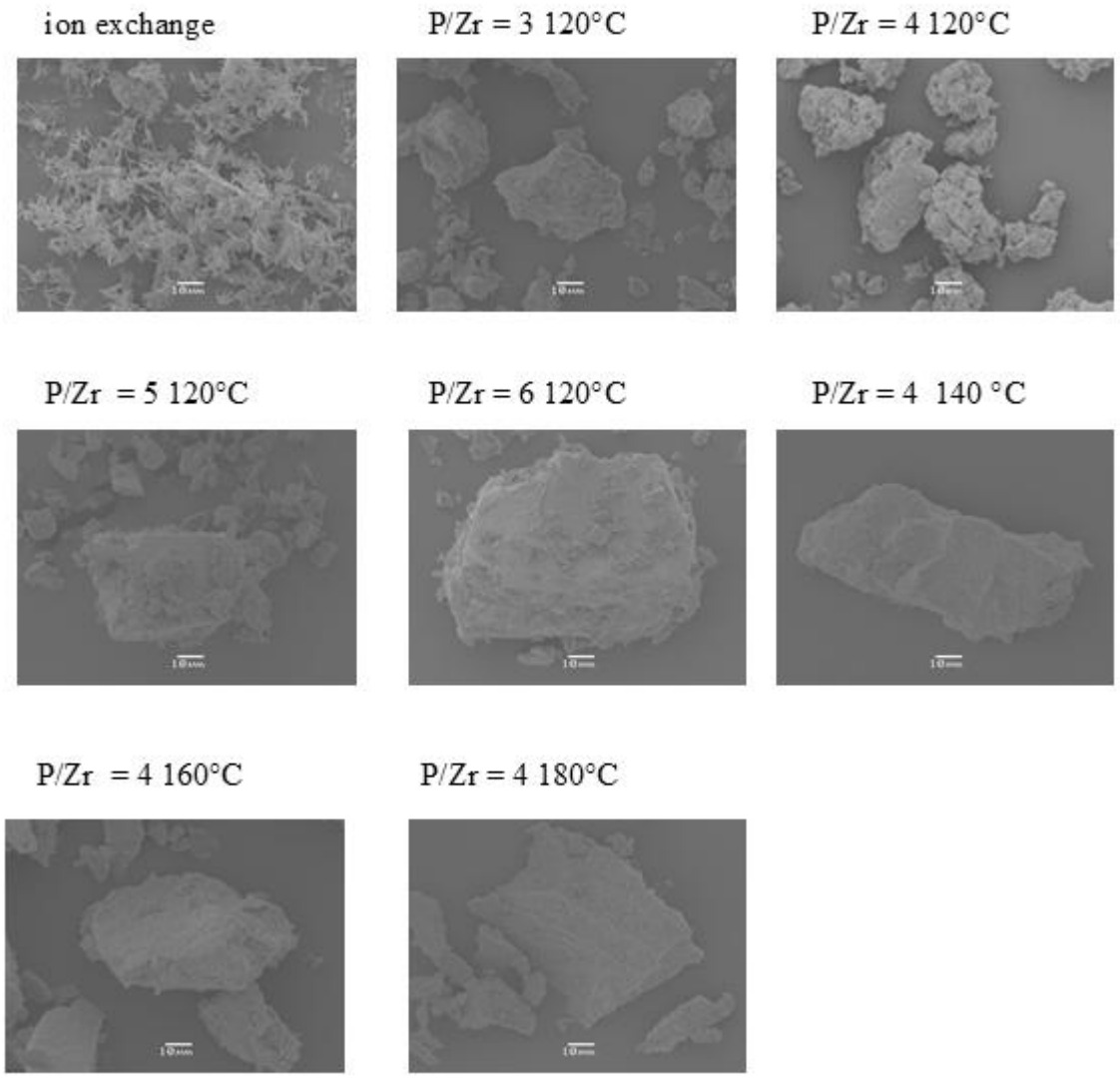

Figure S2. SEM images of ammonium intercalates prepared by ion exchange and by minimal liquid assisted method at various conditions**.**

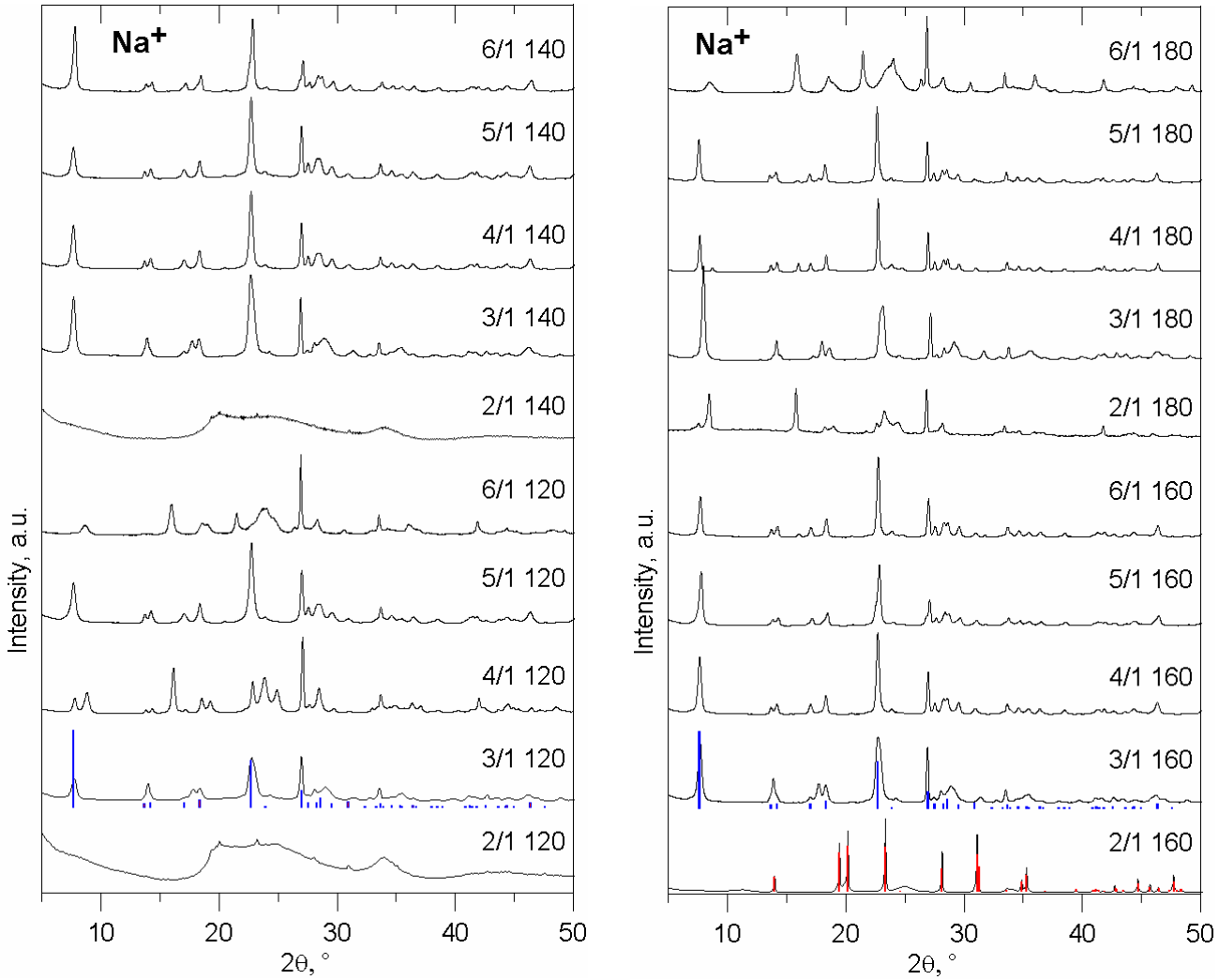

Figure S3. Powder X-ray diffraction patterns of sodium intercalates prepared at various P/Zr ratios and temperatures. Blue lines correspond to indexed pattern of $NaHZr(PO_4)(HPO_4)\cdot 1.4\ H_2O$ prepared by ion exchange, red lines to $NaZr_2(PO_4)_3$ (JCPDS No. 00-035-0756).

Table S2. Powder X-ray diffraction pattern of $Zr(PO_4)(NaHPO_4)\cdot 1.4H_2O$, prepared by ion exchange, indexed in monoclinic cell:

SG = $P2_1$ or $P2_1/m$
a = 11.8439 ± 0.0004 Å
b = 5.3240 ± 0.0002 Å
c = 6.6302 ± 0.0002 Å
β = 102.238 ± 0.005
V = 408.6 ± 0.1 Å^3

2θ	d [Å]	Int.	h	k	l	$2\theta_{exp}-2\theta_{calc}$
7.627	11.58189	100	1	0	0	-0.005
13.649	6.48258	5	0	0	1	-0.007
14.149	6.25435	7	-1	0	1	-0.018
15.300	5.78662	1	2	0	0	0.002
17.010	5.20851	6	1	0	1	-0.017
18.298	4.84454	10	1	1	0	-0.029
21.903	4.05467	1	-1	1	1	-0.015
22.670	3.91923	61	2	0	1	0.021
			2	1	0	-0.006
23.878	3.72354	2	1	1	1	-0.015
26.944	3.30639	22	-1	0	2	0.006
27.495	3.24142	6	0	0	2	-0.015
28.230	3.15862	6	2	1	1	-0.004
28.540	3.12507	12	3	1	0	-0.009
29.510	3.02453	5	-3	1	1	-0.000
30.877	2.89366	8	4	0	0	0.000
32.334	2.76649	1	0	1	2	0.013
33.251	2.69229	1	-2	1	2	0.020
33.647	2.66149	5	0	2	0	0.006
33.883	2.64353	2	3	1	1	-0.017
34.576	2.59207	3	1	2	0	0.030
35.292	2.54112	3	4	1	0	0.018
35.452	2.53003	2	-4	1	1	0.036
36.373	2.46805	3	-3	1	2	0.040
36.654	2.44977	1	-1	2	1	-0.014
37.964	2.36819	1	1	2	1	0.028
38.452	2.33923	2	2	1	2	-0.030
38.871	2.31499	2	5	0	0	-0.001
40.407	2.23043	1	4	1	1	-0.013
40.838	2.20791	1	-1	0	3	0.027
41.176	2.19055	3	3	2	0	0.010
41.408	2.17880	2	-2	0	3	0.035
41.789	2.15982	2	0	0	3	0.000
42.548	2.12303	3	5	1	0	-0.002
43.599	2.07427	1	-1	2	2	-0.014
44.226	2.04630	2	5	0	1	0.013
44.351	2.04084	3	-1	1	3	-0.006
44.917	2.01642	1	-2	1	3	0.034
45.245	2.00255	1	0	1	3	-0.027
			3	2	1	0.028
46.301	1.95932	7	4	2	0	-0.005
47.543	1.91099	1	5	1	1	-0.013

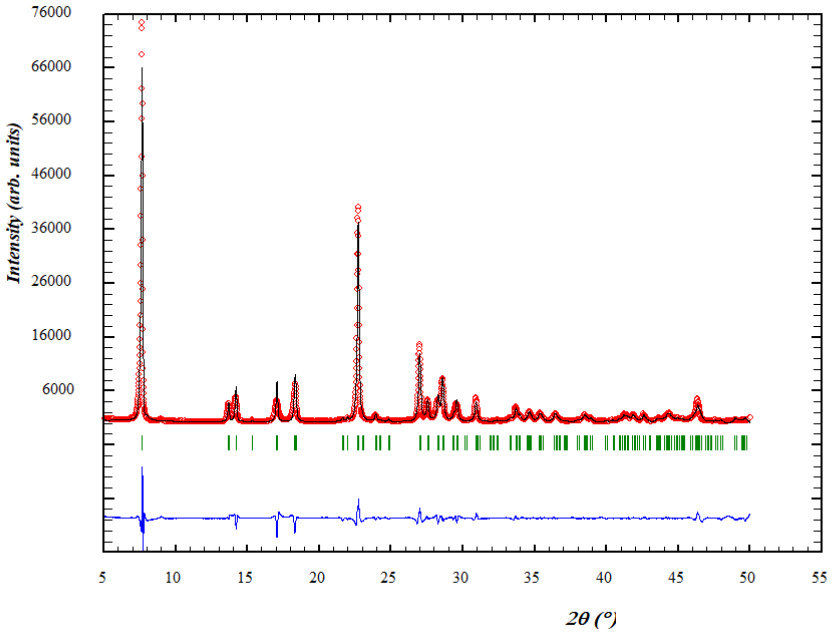

Figure S4. X-Ray powder pattern of Na intercalate with final Le Bail's and difference plots.

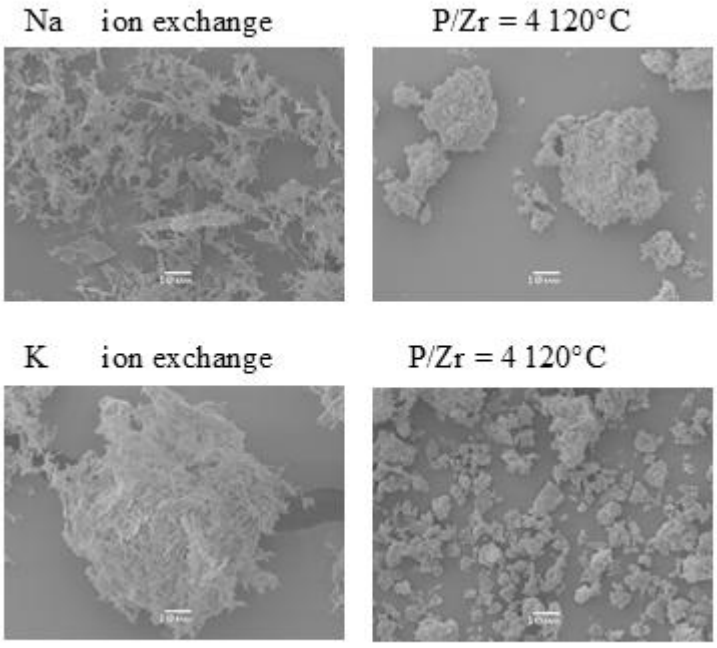

Figure S5. SEM images of sodium and potassium intercalates prepared by ion exchange and by minimal liquid assisted method**.**

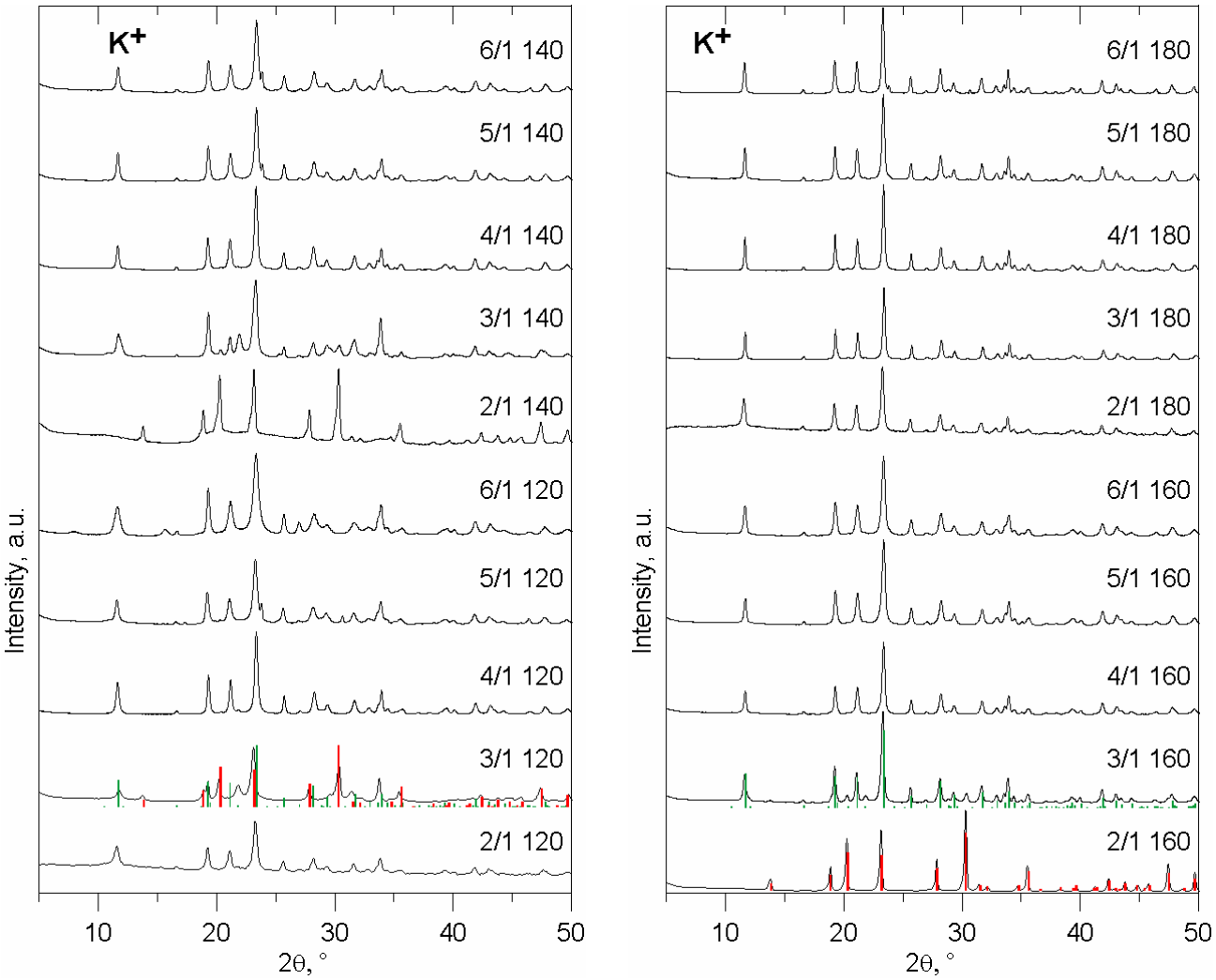

Figure S6. Powder X-ray diffraction patterns of potassium intercalates prepared at various P/Zr ratios and temperatures. Green lines corresponds to $KZrH(PO_4)_2$ (JCPDS No. 04-012-8202), red lines correspond to kosnarite $KZr_2(PO_4)_3$ (JCPDS No. 00-035-0756).

Table S3. Molar ratios P/Zr and M/Zr, and formulas for samples prepared from zirconium propoxide using minimal liquid-assisted method

M	x	P/Zr	M/Zr	H2O wt%	Formula
NH_4	3.5	2.04 ± 0.08	4.66*	0	$NH_4Zr(PO_4)(HPO_4)$
NH_4	3	1.94 ± 0.07	4.59*	0	$NH_4Zr(PO_4)(HPO_4)$
NH_4	2.5	2.05 ± 0.05	4.65*	0	$NH_4Zr(PO_4)(HPO_4)$
NH_4	2	2.10 ± 0.04	4.68*	0	$NH_4Zr(PO_4)(HPO_4)$
NH_4	1.5	1.99 ± 0.08	4.22*	0	$(NH_4)_{0.9}H_{0.1}Zr(PO_4)(HPO_4)$
Na	3.5	1.92 ± 0.10	1.45 ± 0.06	6.5	$Na_{1.4}H_{0.6}Zr(PO_4)(HPO_4)\cdot 1.2H_2O$
Na	3	1.98 ± 0.06	1.19 ± 0.04	7.0	$Na_{1.2}H_{0.8}Zr(PO_4)(HPO_4)\cdot 1.4H_2O$
Na	2.5	2.12 ± 0.07	1.11 ± 0.09	6.2	$Na_{1.1}H_{0.9}Zr(PO_4)(HPO_4)\cdot 1.3H_2O$
Na	2	1.98 ± 0.08	0.95± 0.07	5.6	$NaHZr(PO_4)(HPO_4)\cdot H_2O$
Na	1.5	2.06 ± 0.09	0.67 ± 0.04	7.4	$Na_{0.7}H_{0.3}Zr(PO_4)(HPO_4)\cdot 1.3H_2O$
K	3	1.97 ± 0.05	1.83± 0.02	0	$K_{1.8}H_{0.2}Zr(PO_4)_2$
K	2.5	1.96 ± 0.03	1.28± 0.08	0	$K_{1.3}H_{0.7}Zr(PO_4)_2$
K	2	1.93 ± 0.04	1.17± 0.07	0	$K_{1.2}H_{0.8}Zr(PO_4)_2$
K	1.5	1.93 ± 0.08	0.94± 0.04	0	$K_{0.9}H_{1.1}Zr(PO_4)_2$
K	1	1.98 ± 0.03	0.8± 0.06	0	$K_{0.8}H_{1.2}Zr(PO_4)_2$

* Nitrogen content in wt% in the intercalate determined by organic elemental analysis. The theoretical nitrogen content for the composition γ-$NH_4Zr(PO_4)(HPO_4)$ is 4.67 wt%.

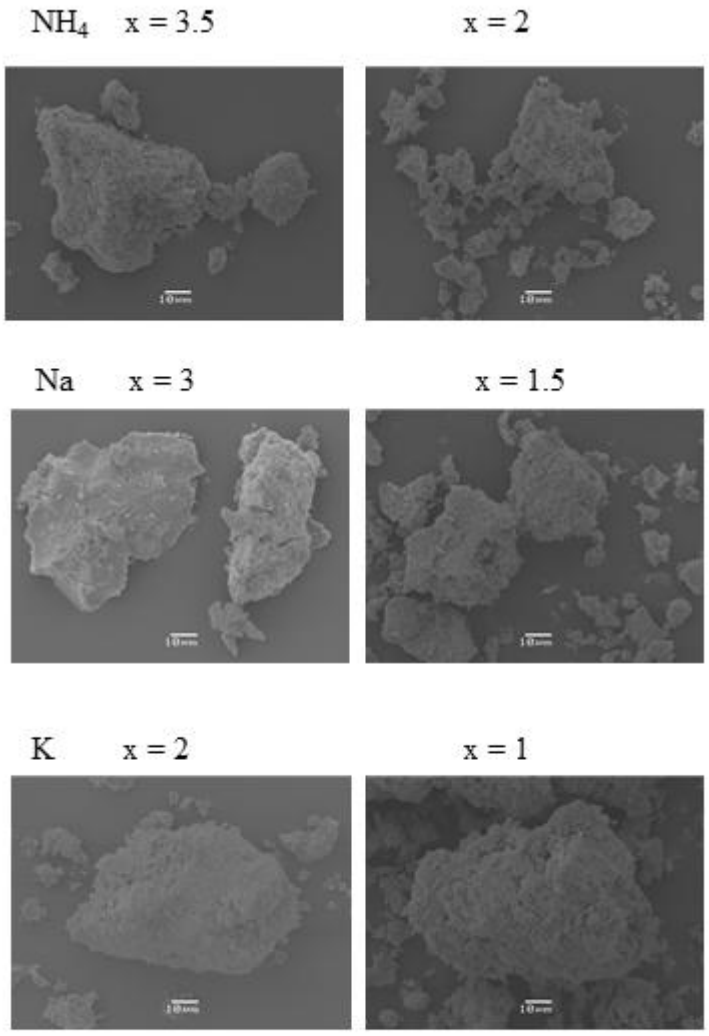

Figure S7. SEM images of ammonium, sodium and potassium intercalates prepared from zirconium propoxide by minimal liquid assisted method with a mixture of MH_2PO_4 and phosphoric acid**.**

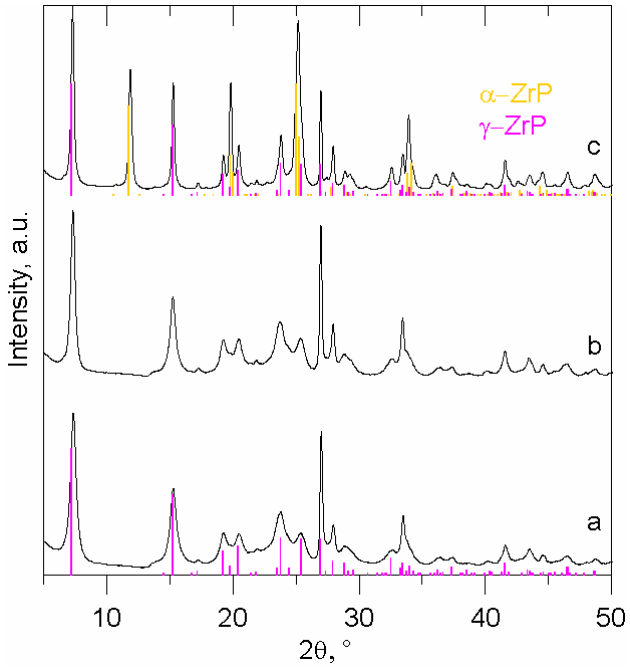

Figure S8. PXRD patterns of HCl-treated ammonium intercalates prepared from propoxide x = 2 (a), propoxide x = 1.5 (b), and oxychloride x = 3 (c).

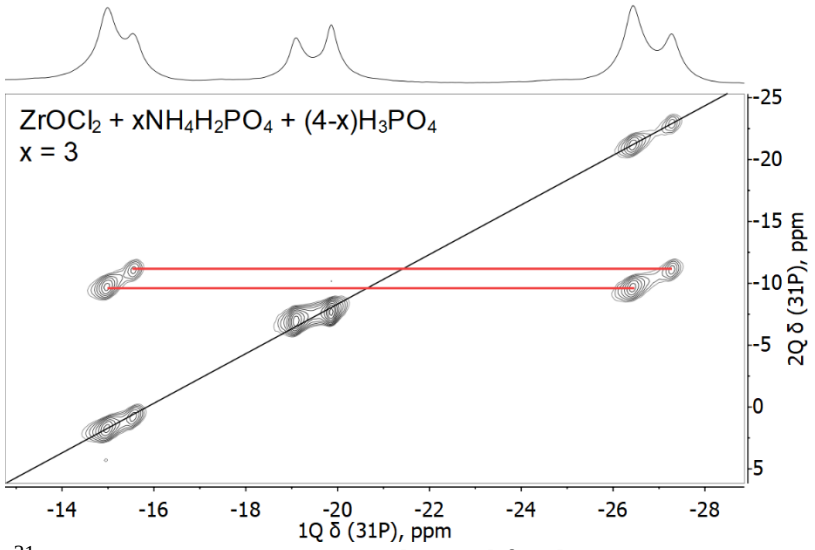

Figure S9. ^{31}P – ^{31}P 1Q – 2Q NMR spectrum obtained for the ammonium intercalate sample synthesized via the zirconium oxychloride route and x = 3.

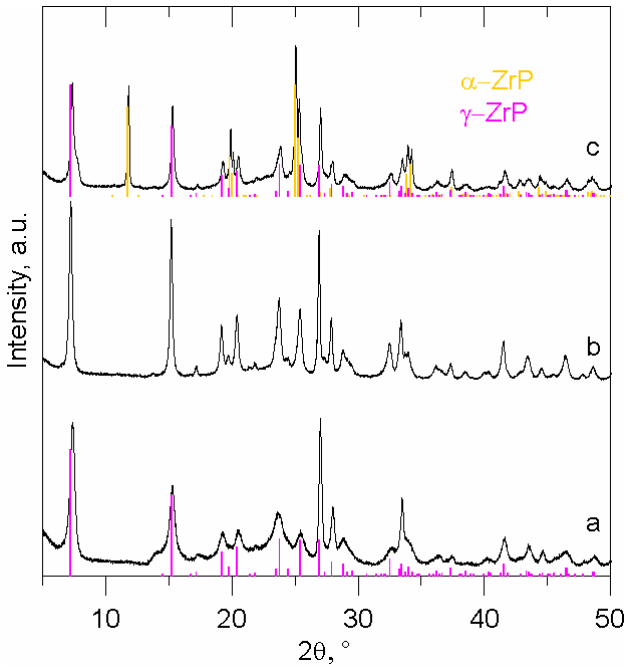

Figure S10. PXRD patterns of HCl-treated sodium intercalates prepared from propoxide x = 2 (a), x = 1.5 (b), and x = 1 (c).

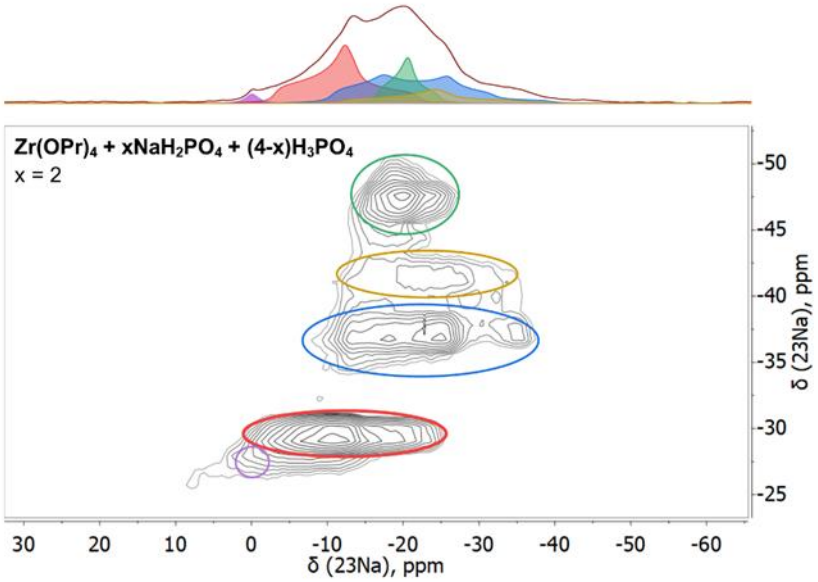

Figure S11. ^{23}Na MQMAS NMR spectrum obtained for the sodium intercalate sample synthesized via the zirconium propoxide route and x = 2. ^{23}Na MAS NMR spectrum and spectral fitting are shown as the projection.

Table S4. Powder X-ray diffraction pattern of $K_{0.9}H_{1.1}Zr(PO_4)_2$ indexed in monoclinic cell:

Monoclinic, SG = $P2_1/a$

a = 9.2028 ± 0.0002 Å
b = 5.2955 ± 0.0001 Å
c = 7.4678 ± 0.0002 Å
β = 94.700 ± 0.004 °

V = 362.71 ± 0.07 Å^3

2θ	d [Å]	Int.	h	k	l	$2\theta_{exp}-2\theta_{calc}$
11.859	7.45663	36	0	0	1	-0.022
19.342	4.58547	60	1	1	0	0.002
			2	0	0	0.002
21.904	4.05457	47	-2	0	1	0.005
23.185	3.83334	100	1	1	1	0.009
25.709	3.46237	1	2	1	0	0.033
29.606	3.01495	17	-2	0	2	-0.020
30.253	2.95194	20	-1	1	2	-0.027
31.547	2.83370	31	1	1	2	-0.003
32.167	2.78051	6	2	0	2	-0.002
33.832	2.64735	78	0	2	0	0.005
			3	1	0	0.005
35.123	2.55295	3	-3	1	1	-0.008
35.990	2.49338	3	0	2	1	0.018
39.296	2.29091	3	2	2	0	0.038
			4	0	0	0.037
40.353	2.23334	6	-3	1	2	0.004
40.571	2.22184	7	-1	1	3	-0.026
41.777	2.16042	10	0	2	2	-0.061
42.826	2.10988	4	2	0	3	0.021
43.223	2.09143	4	3	1	2	-0.064
44.641	2.02824	11	-4	0	2	-0.011
45.545	1.99007	3	-2	2	2	-0.028
47.392	1.91672	17	2	2	2	0.018
48.348	1.88103	2	-3	1	3	-0.081
48.866	1.86230	2	0	0	4	-0.046
52.174	1.75174	7	3	1	3	-0.073
52.776	1.73316	18	1	3	0	0.007
			4	2	0	0.006
			5	1	0	0.005
53.268	1.71830	8	-5	1	1	-0.017
54.500	1.68235	10	1	3	1	0.003
55.110	1.66516	7	4	2	1	0.013
55.655	1.65012	6	2	2	3	0.015
56.786	1.61991	6	-5	1	2	0.003
58.445	1.57782	5	-3	1	4	-0.079
59.099	1.56191	3	1	3	2	0.006
60.541	1.52813	13	3	3	0	0.024
			6	0	0	0.022
61.321	1.51053	4	-3	3	1	-0.039
63.042	1.47338	4	6	0	1	0.019
64.978	1.43408	2	-3	3	2	0.038
			-1	1	5	-0.046
68.374	1.37089	1	5	1	3	0.057

70.280	1.33831	1	-3	1	5	0.027
			2	1	5	-0.015
71.175	1.32367	12	0	4	0	0.013
			6	2	0	0.011
72.447	1.30353	3	0	4	1	-0.007
74.559	1.27174	4	2	4	0	0.014
			5	3	0	0.013
			7	1	0	0.012
75.435	1.25913	3	1	3	4	-0.037
77.920	1.22507	3	-5	3	2	-0.001
78.934	1.21186	1	-5	2	4	0.019
			-2	4	2	0.014
81.237	1.18322	1	5	3	2	-0.004
82.028	1.17380	1	2	0	6	-0.032
		1	4	1	5	0.041
82.282	1.17082	1	-7	1	3	-0.049
83.396	1.15799	1	3	3	4	0.011
86.729	1.12184	2	-8	0	2	-0.001
86.729	1.12184	2	2	4	3	-0.028

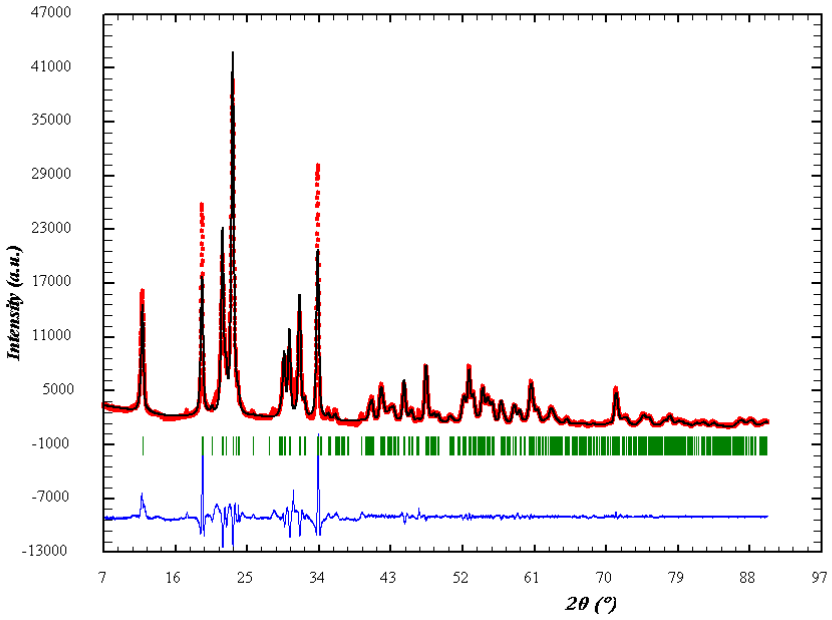

Figure S12. X-ray powder pattern of $K_{0.9}H_{1.1}Zr(PO_4)_2$ with final Le Bail's and difference plots.

Table S5. Powder X-ray diffraction pattern of $K_{0.8}H_{1.2}Zr(PO_4)_2$ indexed in monoclinic cell:

Monoclinic SG = $P2_1/a$

a = 9.2005 ± 0.0002 Å
b = 5.2947 ± 0.0001 Å
c = 7.4628 ± 0.0002 Å
β = 94.677 ± 0.003 °

V = 362.33 ± 0.06 Å^3

2θ	d [Å]	Int.	h	k	l	$2\theta_{exp}$-$2\theta_{calc}$
11.864	7.45326	38	0	0	1	-0.025
19.343	4.58504	61	1	1	0	0.001
			2	0	0	-0.000
21.907	4.05394	52	-2	0	1	-0.003
23.182	3.83383	100	1	1	1	0.001
29.634	3.01216	18	-2	0	2	-0.013
30.267	2.95053	22	-1	1	2	-0.029
31.563	2.83226	32	1	1	2	0.002
32.173	2.77994	6	2	0	2	-0.005
33.832	2.64737	82	0	2	0	-0.000
			3	1	0	-0.003
35.123	2.55292	4	-3	1	1	-0.020
36.014	2.49178	3	0	2	1	0.034
39.302	2.29059	2	2	2	0	0.036
			4	0	0	0.034
40.598	2.22041	8	-1	1	3	-0.025
41.750	2.16178	10	2	2	1	0.089
42.890	2.10692	4	2	0	3	0.067
43.254	2.09001	4	3	1	2	-0.042
44.656	2.02760	13	-4	0	2	-0.021
45.556	1.98961	4	-2	2	2	-0.036
47.392	1.91671	18	2	2	2	0.007
48.346	1.88112	3	4	0	2	0.081
48.899	1.86114	2	0	0	4	-0.046
50.396	1.80929	2	0	2	3	0.010
52.224	1.75017	8	3	1	3	-0.037
52.780	1.73304	18	1	3	0	0.002
			4	2	0	-0.001
			5	1	0	-0.002
53.288	1.71770	10	0	3	1	-0.016
54.493	1.68253	11	-2	1	4	-0.007
			1	3	1	-0.013
55.116	1.66498	7	4	2	1	0.010
55.641	1.65052	5	2	2	3	-0.017
56.797	1.61963	7	-5	1	2	-0.013
57.171	1.60991	3	-4	2	2	-0.025
58.438	1.57800	5	-1	3	2	0.091
59.087	1.56221	4	1	3	2	-0.021
60.540	1.52814	13	3	3	0	0.012
			6	0	0	0.008
61.344	1.51003	4	-3	3	1	-0.032
62.467	1.48556	1	1	2	4	-0.017
			3	3	1	-0.015
63.076	1.47266	5	3	1	4	0.038
64.998	1.43370	2	-3	3	2	0.035
65.924	1.41578	1	2	2	4	0.023
66.894	1.39758	1	1	1	5	0.042
68.385	1.37071	1	5	1	3	0.052
70.271	1.33847	1	-3	1	5	-0.039
71.169	1.32376	12	0	4	0	-0.005
71.169	1.32376	12	6	2	0	-0.011
74.102	1.27846	1	3	3	3	-0.032
74.575	1.27151	3	-2	2	5	0.021

			1	2	5	0.007
			2	4	0	0.015
			5	3	0	0.012
			7	1	0	0.009
74.949	1.26609	2	-5	3	1	-0.045
75.427	1.25925	3	-4	1	5	0.043
			3	1	5	0.012
77.923	1.22503	3	-5	3	2	0.021
78.900	1.21230	2	-2	4	2	-0.043
79.331	1.20680	1	0	1	6	0.017
81.219	1.18343	1	5	3	2	-0.037
82.033	1.17374	1	4	1	5	0.014
83.420	1.15771	1	-5	3	3	0.064
			3	3	4	0.009
86.760	1.12152	2	-8	0	2	-0.009
			2	4	3	-0.021
89.854	1.09076	1	-7	1	4	-0.011

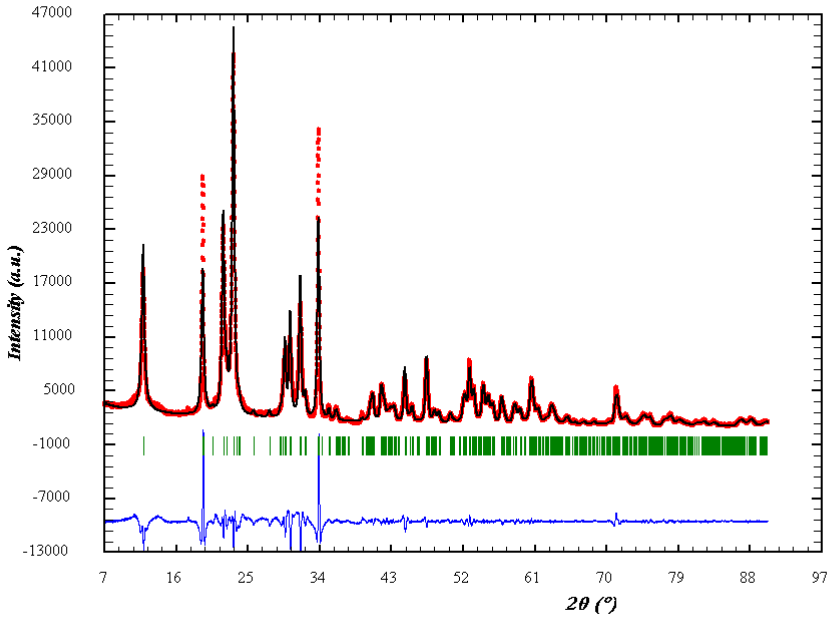

Figure S13. X-ray powder pattern of $K_{0.8}H_{1.2}Zr(PO_4)_2$ with final Le Bail's and difference plots.

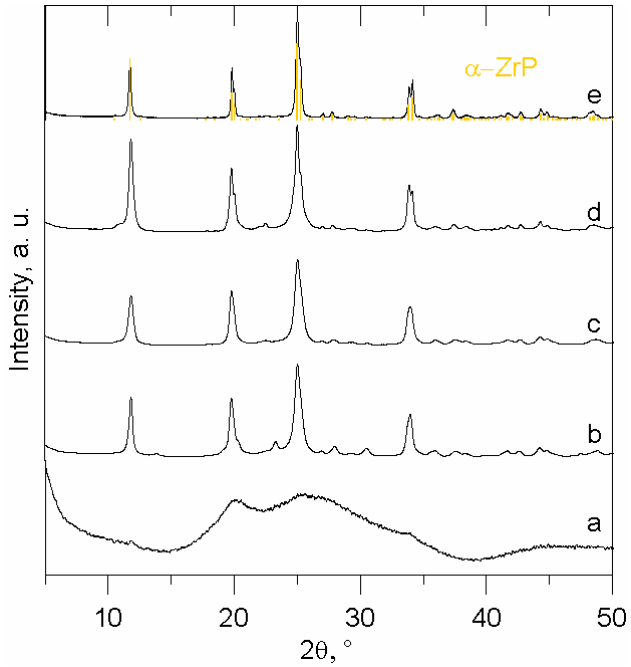

Figure S14. PXRD patterns of HCl-treated potassium intercalates prepared from propoxide x = 3 (a), x = 2.5 (b), x = 1.5 (c), and oxychloride x = 2.5 (d), x = 1.5 (e).

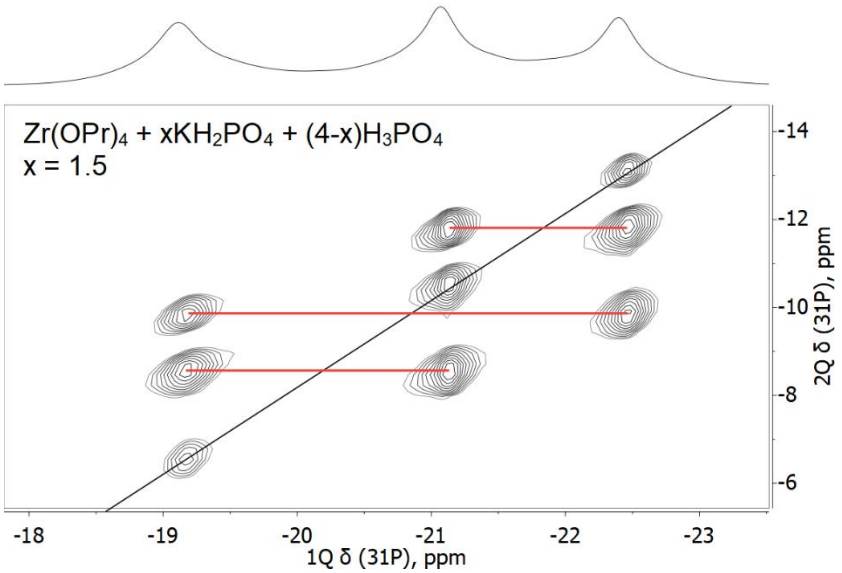

Figure S15. ^{31}P – ^{31}P 1Q – 2Q NMR spectrum obtained for the potassium intercalate sample synthesized via the zirconium propoxide route and x = 1.5.