Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Yasuaki Matsuda,[a] Masao Yonemura,[b] Hikaru Koga,[a] Cedric Pitteloud,[a] Miki Nagao,[b] Masaaki Hirayama[a] and Ryoji Kanno*[a]

a) Department of Electronic Chemistry, Interdisciplinary Graduate School of science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, Kanagawa 226-8502, Japan.
b) Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 203-1 Shirakata, Tokai, Ibaraki 319-1106, Japan.

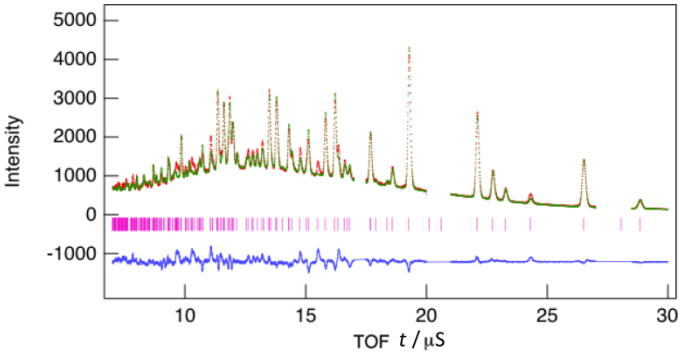

Fig. S1 Neutron Rietveld refinement patterns for $RbMg_{0.9}H_{0.2}(PO_3)_3{\cdot}yH_2O$ at 453 K.

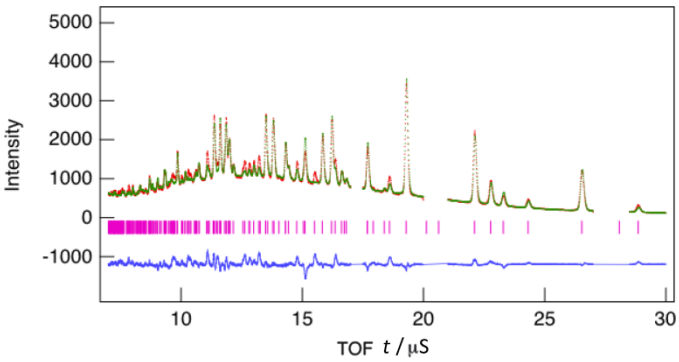

Fig. S2 Neutron Rietveld refinement patterns for $RbMg_{0.9}H_{0.2}(PO_3)_3{\cdot}yH_2O$ at 553 K.

Table S1. Crystallographic Data for $RbMg_{0.9}H_{0.2}(PO_3)_3{\cdot}yH_2O$ at 298 K.

Formula sum	$RbMg_{0.9}H_{0.2}(PO_3)_3{\cdot}1.4H_2O$
Formula weight	371.48
Crystal system	Rhombohedral
Space group	*R32*
Cell parameters	a = 10.2402 Å, c = 7.1762 Å
V	651.69 $Å^3$
Z	3
Calc. density	2.861 g cm^{-3}

Table S2 Rietveld refinement results for $RbMg_{0.9}H_{0.2}(PO_3)_3 \cdot 1.4H_2O$ at 298 K.

Atom	Site	*q*	*x*	*y*	*z*	*U* / Å^2
Mg	3*a*	0.9	0	0	0	0.0073(7)
Rb	3*b*	1	0	0	0.5	0.0079(7)
P	9*e*	1	0.4329(2)	0	0.5	0.0126(7)
O(1)	18*f*	1	0.1876(13)	0.0889(2)	0.1670(4)	0.0211(6)
O(2)	9*e*	1	0.3498(3)	0	0	0.0394(9)
O(3)	18*f*	0.237(4)	0.233(10)	0.2871(9)	0.149(13)	0.0335
H(1)	18*f*	0.146(7)	0.145(3)	0.238(3)	0.114(4)	0.044(8)
H(2)	18*f*	0.279(6)	0.779(15)	0.080(19)	0.236(12)	0.043(4)
H(3)	9*d*	0.41(10)	0.777(1110)	0	0	0.034(4)

Atom	U_{11}/ Å^2	U_{33} / Å^2	U_{12} / Å^2	U_{13} / Å^2	U_{23} / Å^2	U_{22} / Å^2
O(3)	0.014(4)	0.029(7)	0.063(10)	0.014(4)	0.007(5)	0.0017(5)

Space group *R32*, a = 10.2402(13) Å, c = 7.1762(15) Å, R_{wp} = 6.90 %, R_p = 4.77 %.

Table S3 Rietveld refinement results for $RbMg_{0.9}H_{0.2}(PO_3)_3 \cdot 1.3H_2O$ at 453 K.

Atom	Site	*q*	*x*	*y*	*z*	*U* / Å^2
Mg	3*a*	0.9	0	0	0	0.013(14)
Rb	3*b*	1	0	0	0.5	0.013(12)
P	9*e*	1	0.4324(4)	0	0.5	0.0154(9)
O(1)	18*f*	1	0.18714(2)	0.0879(3)	0.1665(6)	0.0260(7)
O(2)	9*e*	1	0.3486(4)	0	0	0.042(9)
O(3)	18*f*	0.216(5)	0.236(2)	0.287(18)	0.150(2)	0.0436
H(1)	18*f*	0.106(7)	0.121(3)	0.211(3)	0.143(6)	0.046(9)
H(2)	18*f*	0.204(6)	0.765(3)	0.077(3)	0.223(2)	0.079(6)
H(3)	9*d*	0.40(13)	0.779(19)	0	0	0.039(5)

Atom	U_{11}/Å^2	U_{22}/Å^2	U_{33}/Å^2	U_{12}/Å^2	U_{13}/Å^2	U_{23}/Å^2
O(3)	0.021(5)	0.027(8)	0.08(10)	0.014(6)	0.008(7)	0.005(7)

Space group *R32*, a = 10.2532(18) Å, c = 7.1955(2) Å, R_{wp} = 6.52 %, R_p = 4.75 %.

Table S4 Rietveld refinement results for $RbMg_{0.9}H_{0.2}(PO_3)_3 \cdot 1.0H_2O$ at 453 K.

Atom	Site	*q*	*x*	*y*	*z*	*U* / Å^2
Mg	3*a*	0.9	0	0	0	0.016(16)
Rb	3*b*	1	0	0	0.5	0.015(14)
P	9*e*	1	0.4336(4)	0	0.5	0.017(12)
O(1)	18*f*	1	0.1880(3)	0.0904(3)	0.1662(8)	0.0302 (7)
O(2)	9*e*	1	0.3475(4)	0	0	0.052(13)
O(3)	18*f*	0.171(4)	0.249(3)	0.319(3)	0.138(3)	0.0694
H(2)	18*f*	0.131(6)	0.74(10)	0.083(8)	0.116(5)	0.13(10)

Atom	U_{11}/Å^2	U_{22}/Å^2	U_{33}/Å^2	U_{12}/Å^2	U_{13}/Å^2	U_{23}/Å^2
O(3)	0.034(9)	0.06(15)	0.09(10)	0.005(9)	-0.011(14)	0.012(19)

Space group *R32*, a =10.2599(19) Å, c = 7.2060(2) Å, R_{wp} = 6.35 %, R_p = 4.49 %.

Note : The form of the anisotropic temperature factor is $\exp[-2p^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{11} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Table S5. Interatomic distance (Å), bond angles (°) for $RbMg_{0.9}H_{0.2}(PO_3)_3 \cdot yH_2O$

Temperature T / K	298	453	553
Interatomic distance	l / Å	l / Å	l / Å
Mg^a – $O(1)^a$	2.012	2.049	2.056
Rb^a – $O(1)^a$	2.912	2.919	2.929
P^b – $O(1)^a$	1.441	1.442	1.443
P^b – $O(2)^a$	1.634	1.630	1.635
$O(1)^a$ – $H(1)^a$	1.825	1.811	
$O(1)^c$ – $H(1)^d$	2.090	2.253	
$O(1)^a$ – $H(2)^e$	1.828	1.769	1.669
$O(1)^a$ – $H(2)^f$	1.361	1.466	1.591
$O(1)^a$ – $H(3)^f$	1.719	1.715	
$O(3)^a$ – $H(1)^{\#1}$	0.817	1.026	
$O(3)^a$ – $H(2)^g$	1.343	1.258	1.376
$O(3)^a$ – $H(2)^e$	1.604	1.429	1.429
$O(3)^d$ – $H(2)^f$	1.910	1.972	1.839
$O(3)^a$ – $H(3)^f$	1.232	1.242	
Bond angle	ϕ / °	ϕ / °	ϕ / °
$O(1)^a$ – P^b – $O(1)^g$	127.58	127.87	124.09
$O(2)^a$ – P^b – $O(2)^h$	94.97	95.62	97.43
$O(1)^g$ – P^b – $O(2)^h$	112.35	111.67	112.14
$O(1)^a$ – P^b – $O(2)^h$	102.52	102.77	104.00
$H(1)^a$ – $O(1)^a$ – $H(2)^f$	71.73	73.36	
$H(1)^a$ – $O(1)^a$ – $H(2)^e$	73.62	77.84	
$H(1)^d$ – $O(1)^g$ – $H(3)^i$	35.24	40.14	
$H(1)^a$ – $O(1)^a$ – $H(3)^f$	39.63	48.56	
$H(2)^e$ – $O(1)^a$ – $H(2)^f$	38.87	30.31	26.00
$H(2)^f$ – $O(1)^a$ – $H(3)^f$	74.06	69.54	
$H(2)^e$ – $O(1)^a$ – $H(3)^f$	50.10	49.68	
$H(1)^a$ – $O(3)^a$ – $H(2)^f$	121.34	119.52	
$H(1)^a$ – $O(3)^a$ – $H(2)^e$	125.84	132.04	
$H(1)^a$ – $O(3)^a$ – $H(3)^f$	68.59	79.01	
$H(2)^e$ – $O(3)^a$ – $H(2)^f$	44.80	38.23	30.29
$H(2)^f$ – $O(3)^a$ – $H(3)^f$	93.49	93.80	
$H(2)^e$ – $O(3)^a$ – $H(3)^f$	62.49	66.05	
$H(2)^f$ – $O(3)^d$ – $H(3)^i$	52.00	47.86	

Symmetry codes: [a]x, y, z, [b]-y+1/3, x-y+2/3, z+2/3, [c]-y+2/3, -x+y+1/3, z+2/3, [d]-y+2/3, x-y+1/3, z+1/3, [e]x-y+2/3, -y+1/3, -z+1/3, [f]-x+y, -x, z [g]-x+2/3, -x+y+1/3, -z+1/3, [h]-x+y+2/3, -x+1/3, z+1/3, [i]x+2/3, y+1/3, z+1/3