Supplementary information

Crystal chemistry and physical properties of the A2M3(H2O)2[B4P6O24(OH)2] (A = Cs, Rb; M = Ni, Cu, (Ni, Fe)) borophosphate family

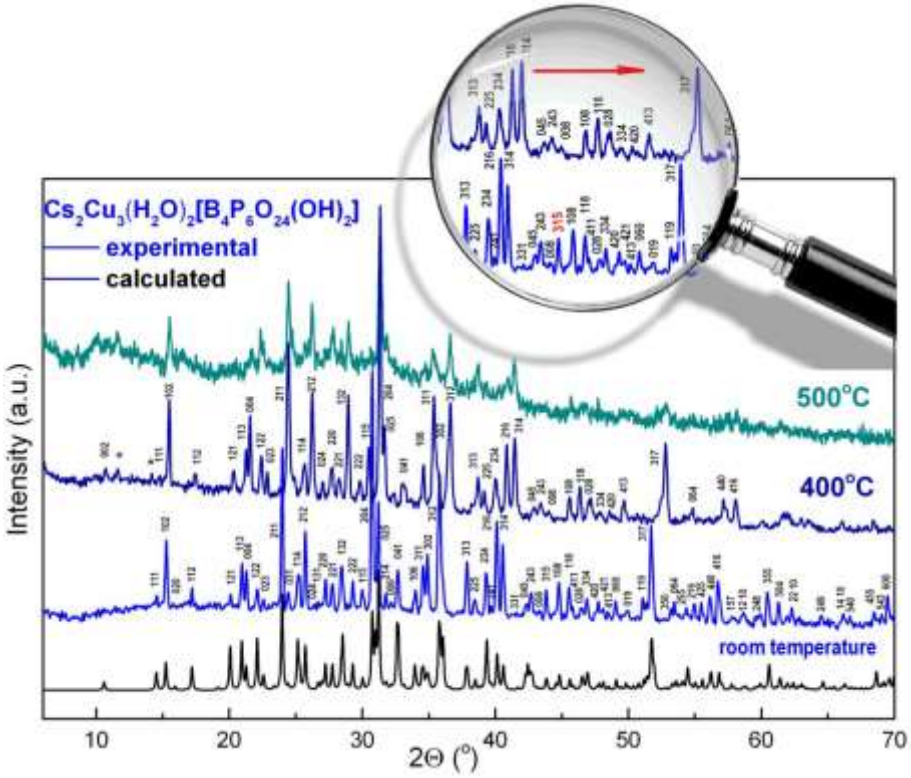
Shvanskaya Larisa, *[a,b] Yakubovich Olga,[a] Melchakova Lyubov, [a] Ivanova Anna[c] and Vasiliev Alexander [a,b,d]

[a]*M.V. Lomonosov Moscow State University, Leninskie Gory, GSP-1, Moscow, 119991, Russian Federation.*

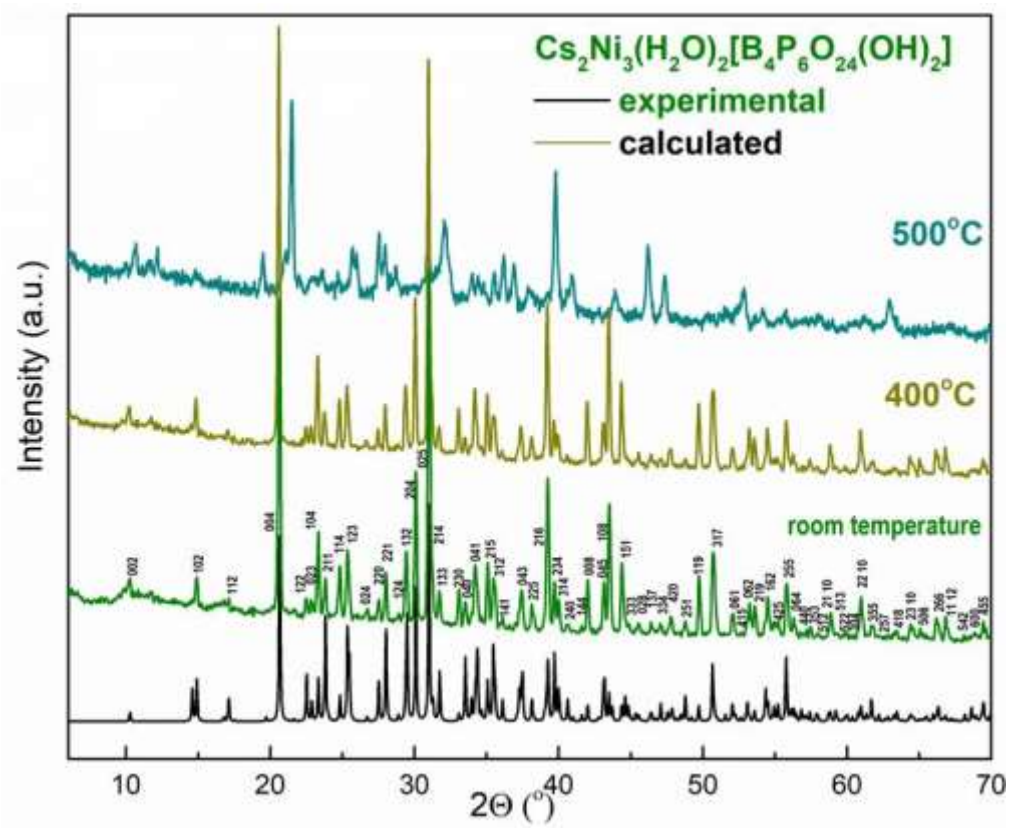
[b]*National University of Science and Tehnology "MISiS", Leninskiy prospekt, 4, Moscow, 119049, Russian Federation.*

[c]*Shubnikov Institute of Crystallography, RAS, Moscow, Russia.*

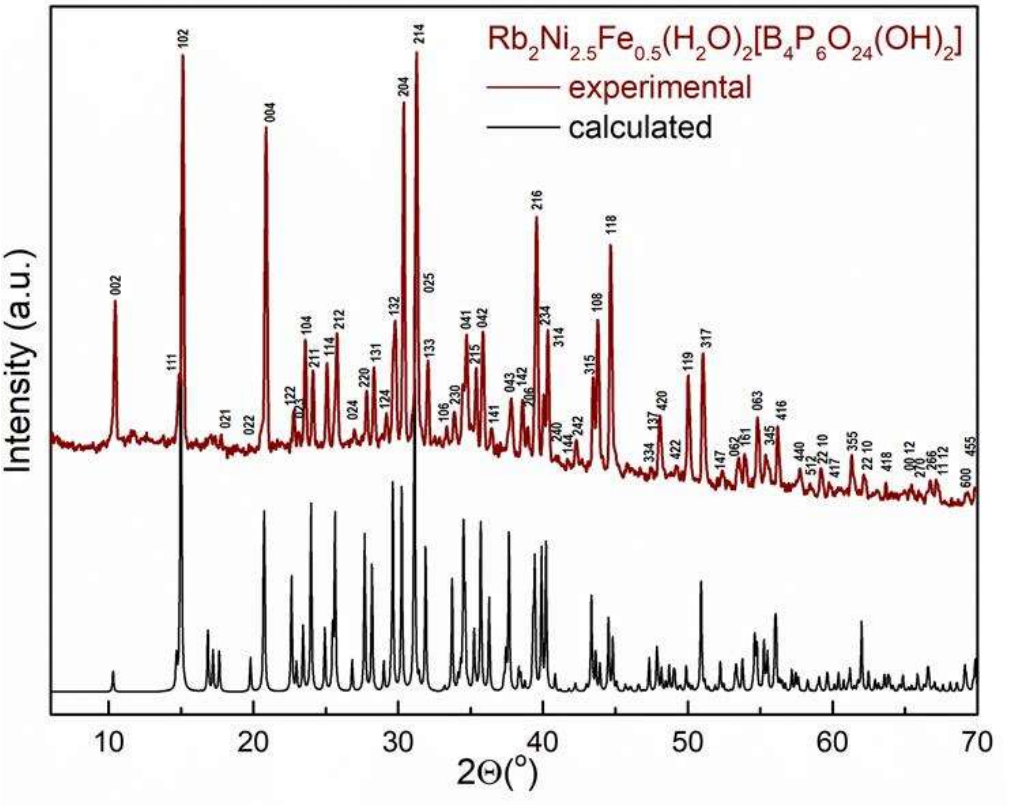
[d]*National Research South Ural State University, Chelyabinsk 454080, Russia*



a



b



c

Fig. S1. PXRD patterns for the simulated based on the x-ray single crystal diffraction and the experimental samples of $A_2M_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$, where *A*=Cs, Rb; *M*=Ni, Cu, (Ni,Fe). X-ray diffraction patterns of samples annealed at 400°C and 500°C are also presented (*a*,*b*).

Table S1. Atomic coordinates and isotropic/equivalent isotropic displacement parameters ($Å^2$) for (I)

Atom	Wyck.	x/a	y/b	z/c	Uiso/Ueq
Cs1	8c	0.35065(15)	0.08072(11)	0.14780(6)	0.0311(2)
Cs2	8c	0.3057(4)	0.0979(3)	0.1543(2)	0.0311(2)
Cs3	8c	0.3332(7)	0.0984(4)	0.1346(2)	0.0311(2)
Cu1	8c	0.68366(5)	0.29940(4)	0.08147(2)	0.00971(12)
Cu2	4a	½	0	½	0.01583(18)
P1	8c	0.50040(11)	0.33388(7)	0.21308(4)	0.0071(2)
P2	8c	0.27266(12)	0.05700(8)	0.37681(5)	0.0094(2)
P3	8c	0.50538(11)	0.27467(8)	0.45452(5)	0.0114(2)
O1	8c	0.5071(3)	0.3059(2)	0.13805(12)	0.0097(6)
O2	8c	0.5721(3)	0.1888(2)	0.49617(13)	0.0127(6)
O3	8c	0.4895(3)	0.23551(19)	0.25747(12)	0.0085(5)
O4	8c	0.2963(3)	0.2997(2)	0.32923(12)	0.0101(6)
O5	8c	0.3646(3)	0.3968(2)	0.22630(12)	0.0101(6)
O6	8c	0.6274(3)	0.4003(2)	0.23542(12)	0.0102(6)
O7	8c	0.5255(3)	0.2511(2)	0.37682(13)	0.0172(7)
O8	8c	0.3519(3)	0.2913(2)	0.47306(13)	0.0197(7)
O9	8c	0.1871(3)	-0.0147(2)	0.32821(13)	0.0141(6)
O10	8c	0.1653(3)	0.1249(2)	0.41182(13)	0.0155(6)
O11	8c	0.3605(3)	-0.0083(2)	0.42494(13)	0.0177(7)
O12	8c	0.3700(3)	0.1215(2)	0.32937(15)	0.0206(7)
O13	8c	0.5907(3)	0.3772(2)	0.46520(14)	0.0200(7)
O14	8c	0.3606(3)	0.0552(2)	0.56421(14)	0.0190(7)
B1	8c	0.4158(5)	0.2289(3)	0.3252(2)	0.0092(9)
B2	8c	0.2767(5)	0.3931(3)	0.2887(2)	0.0083(9)
H1	8c	0.282(5)	0.077(6)	0.541(4)	0.10(2)
H2	8c	0.416(7)	0.096(5)	0.592(3)	0.10(2)
H3	8c	0.611(6)	0.378(4)	0.5115(8)	0.051(17)

Site occupations: Cs1 0.673(9), Cs2 0.155(7), 0.172(9).

Table S2. Atomic coordinates and isotropic/equivalent isotropic displacement parameters ($Å^2$) for (II)

Atom	Wyck.	x/a	y/b	z/c	Uiso/Ueq
Cs1	8c	0.3498(3)	0.0896(2)	0.14664(11)	0.0297(4)
Cs2	8c	0.3042(4)	0.1071(4)	0.1583(3)	0.0297(4)
Cs3	8c	0.3347(13)	0.1047(10)	0.1352(5)	0.0297(4)
Ni1	8c	0.68817(8)	0.31233(6)	0.08157(4)	0.00351(19)
Ni2	4a	½	0	½	0.0090(3)
P1	8c	0.51497(16)	0.34053(13)	0.21681(8)	0.0029(3)
P2	8c	0.27410(17)	0.06351(13)	0.37742(8)	0.0036(3)
P3	8c	0.51049(17)	0.27543(14)	0.45528(9)	0.0070(4)
O5	8c	0.3832(4)	0.4094(3)	0.2305(2)	0.0054(6)
O1	8c	0.5157(4)	0.3101(3)	0.1437(2)	0.0054(9)
O2	8c	0.5659(5)	0.1759(4)	0.4937(2)	0.0089(10)
O3	8c	0.5035(5)	0.2385(3)	0.2617(2)	0.0054(6)
O4	8c	0.3098(4)	0.3064(4)	0.3294(2)	0.0066(9)
O6	8c	0.6441(4)	0.4087(4)	0.2370(2)	0.0069(9)
O7	8c	0.5347(4)	0.2600(4)	0.3789(2)	0.0096(7)
O8	8c	0.3618(5)	0.3035(4)	0.4733(2)	0.0130(10)

O9	8c	0.1781(5)	0.0012(4)	0.3287(2)	0.0096(7)
O10	8c	0.1817(5)	0.1452(4)	0.4126(2)	0.0084(9)
O11	8c	0.3425(5)	-0.0170(4)	0.4259(2)	0.0071(9)
O12	8c	0.3875(5)	0.1203(4)	0.3354(3)	0.0132(11)
O13	8c	0.6090(5)	0.3756(4)	0.4694(2)	0.0139(11)
O14	8c	0.3626(5)	0.0481(4)	0.5694(2)	0.0124(10)
B1	8c	0.4299(7)	0.2340(6)	0.3276(4)	0.0040(10)
B2	8c	0.2908(7)	0.4024(6)	0.2894(4)	0.0040(10)
H1	8c	0.280(4)	0.075(6)	0.555(4)	0.02(2)
H2	8c	0.393(13)	0.104(7)	0.595(5)	0.10(5)
H3	8c	0.637(12)	0.367(10)	0.5121(19)	0.08(4)

Site occupations: Cs1 0.62(2), Cs2 0.22(1), 0.16(2).

Table S3. Atomic coordinates and isotropic/equivalent isotropic displacement parameters (Å2) for (IV)

Atom	Wyck.	x/a	y/b	z/c	U_{iso}/U_{eq}
Rb1	8c	0.36831(19)	0.07736(14)	0.14735(9)	0.0460(4)
Rb2	8c	0.2933(10)	0.1051(8)	0.1626(5)	0.0460(4)
Rb3	8c	0.3371(12)	0.1071(9)	0.1243(6)	0.0460(4)
Ni1	8c	0.68168(9)	0.30809(7)	0.08130(4)	0.0062(2)
Ni2	4a	½	0	½	0.0091(3)
Fe2	4a	½	0	½	0.0091(3)
P1	8c	0.50404(19)	0.33663(14)	0.21460(8)	0.0060(4)
P2	8c	0.27314(18)	0.05923(15)	0.37811(8)	0.0065(4)
P3	8c	0.5067(2)	0.27788(15)	0.45384(8)	0.0087(4)
O5	8c	0.3694(5)	0.4040(4)	0.2280(2)	0.0077(10)
O1	8c	0.5061(5)	0.3047(4)	0.1422(2)	0.0082(10)
O2	8c	0.5636(5)	0.1790(4)	0.4924(2)	0.0122(11)
O3	8c	0.4960(5)	0.2349(4)	0.2601(2)	0.0087(10)
O4	8c	0.3006(5)	0.3006(4)	0.3279(2)	0.0071(10)
O6	8c	0.6324(5)	0.4080(4)	0.2343(2)	0.0108(8)
O7	8c	0.5307(5)	0.2651(4)	0.3770(2)	0.0133(11)
O8	8c	0.3575(5)	0.3036(4)	0.4723(2)	0.0134(8)
O9	8c	0.1805(5)	-0.0033(4)	0.3276(2)	0.0100(10)
O10	8c	0.1763(5)	0.1403(4)	0.4131(2)	0.0134(8)
O11	8c	0.3436(5)	-0.0213(4)	0.4262(2)	0.0091(10)
O12	8c	0.3891(5)	0.1175(4)	0.3379(2)	0.0108(8)
O13	8c	0.6026(6)	0.3806(4)	0.4684(2)	0.0161(12)
O14	8c	0.3578(5)	0.0435(5)	0.5703(2)	0.0163(12)
B1	8c	0.4247(8)	0.2316(7)	0.3274(4)	0.0069(12)
B2	8c	0.2814(8)	0.3985(7)	0.2888(4)	0.0069(12)
H1	8c	0.278(6)	0.073(8)	0.551(4)	0.06(3)
H2	8c	0.401(9)	0.096(6)	0.596(4)	0.05(3)
H3	8c	0.633(9)	0.386(7)	0.5121(15)	0.04(3)

Site occupations: Rb1 0.744(7), Cs2 0.127(4), 0.129(7), Ni2 0.50(3), Fe2 0.50(3).

Table S4. Local bond-valence balance in the crystal structures of $A_2M_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$, where *A*=Cs, Rb; *M*=Ni, Cu, (Ni,Fe).

$Cs_2Cu_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$												
	Cu1	Cu2	Cs1*	P1	P2	P3	B1	B2	H1	H2	H3	∑
O1	0.429		0.101	1.368						0.24		**2.14**
O2	0.462	$0.099\downarrow_2^*$				1.361						**1.92**
O3			0.121	1.235			0.729					**2.09**
O4	0.387						0.803	0.803				**1.99**
O5			0.058	1.245				0.774				**2.08**
O6			0.103	1.255				0.737				**2.10**
O7						1.202	0.776					**1.98**
O8	0.541		0.026			1.361						**1.93**
O9			0.065		1.205			0.794				**2.06**
O10	0.205		0.112		1.368						0.42	**2.11**
O11	0.102	$0.465\downarrow_2$			1.350							**1.92**
O12			0.045		1.221		0.795					**2.06**
O13			0.059			1.157			0.20		0.58	**2.00**
O14		$0.489\downarrow_2$	0.155						0.80	0.76		**2.20**
∑	**2.13**	**2.11**	**0.85**	**5.10**	**5.14**	**5.08**	**3.10**	**3.11**	**1.00**	**1.00**	**1.00**	
$Cs_2Ni_3(H_2O)_2[B_4P_6O_{24}(OH)_2]$												
	Ni1	Ni2	Cs1*	P1	P2	P3	B1	B2	H1	H2	H3	∑
O1	0.336		0.146	1.350						0.22		**2.05**
O2	0.292	0.200				1.251						**1.74**
O3			0.098	1.228			0.723					**2.05**
O4	0.282						0.808	0.846				**1.94**
O5			0.117	1.235				0.715				**1.94**
O6			0.047	1.241				0.765				**2.07**
O7			0.032			1.182	0.778					**1.99**
O8	0.408		0.031			1.368						**1.81**
O9			0.081		1.238			0.759				**2.08**
O10	0.341		0.063		1.350						0.45	**2.20**
O11	0.287	$0.287\downarrow_2$			1.269							**1.84**
O12					1.251		0.790					**2.04**
O13			0.051			1.135			0.22		0.55	**1.96**
O14		$0.398\downarrow_2$	0.180						0.78	0.78		**2.14**
∑	**1.95**	**1.77**	**0.85**	**5.05**	**5.05**	**4.94**	**3.10**	**3.09**	**1.00**	**1.00**	**1.00**	
$Rb_2Ni_{2.5}Fe_{0.5}(H_2O)_2[B_4P_6O_{24}(OH)_2]$												
	Ni1	$(Ni_{0.5}Fe_{0.5})2$	Rb1*	P1	P2	P3	B1	B2	H1	H2	H3	∑
O1	0.337		0.114	1.402						0.20		**2.05**
O2	0.300	$0.210\downarrow_2$				1.275						**1.79**
O3			0.081	1.231			0.702					**2.01**
O4	0.276						0.817	0.839				**1.93**
O5			0.037	1.235				0.761				**2.03**
O6			0.095	1.218				0.731				**2.04**
O7						1.186	0.771					**1.96**
O8	0.396					1.402						**1.80**
O9			0.090		1.241			0.761				**2.09**
O10	0.341		0.071		1.310						0.45	**2.17**
O11	0.230	$0.332\downarrow_2$			1.279							**1.84**
O12					1.258		0.817					**2.08**
O13			0.054			1.120			0.23		0.55	**1.95**
O14		$0.425\downarrow_2$	0.13						0.77	0.80		**2.15**
∑	**1.88**	**1.93**	**0.67**	**5.09**	**5.09**	**4.98**	**3.11**	**3.09**	**1.00**	**1.00**	**1.00**	

*The $\downarrow_2$ sign indicate the doubling of the corresponding contributions due to the symmetry. **Taking into account the site with maximum population only, *A*1.

Table S5. Chemical composition of sample (III) determined by EDS analysis

Element/At.%				average
Rb	4,3(1)	4,2(1)	4,2(1)	4.2(1)
Ni	5,7(1)	5,7(1)	5,6(1)	5.7(1)
Fe	1.1(1)	1.2(1)	1.1(1)	1.1(1)
P	14,2(1)	14,4(1)	14,3(1)	14.3(1)
O	62,5(2)	63,5(2)	63,5(2)	63.2(2)