SUPPORTING INFORMATIONS

Novel bismuth oxosalts, β-$Bi_3O_3(VO_4)$ and $KBi_5O_5(PO_4)_2$: synthesis and effect of hydrothermal pressure on the crystal structure

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1. Images of crystals

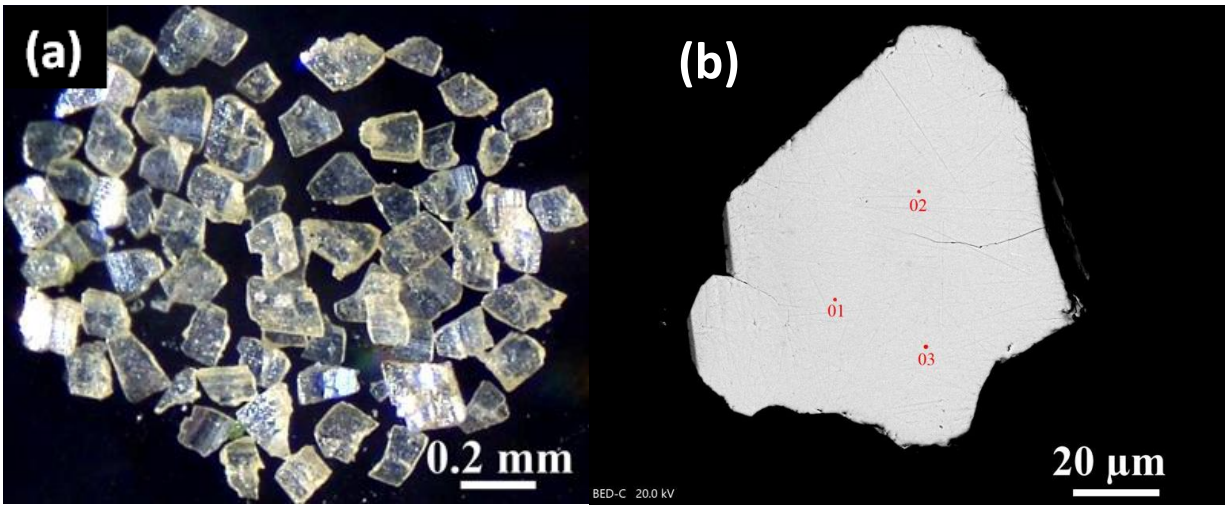

Figure S1. Plate-like crystals of β-$Bi_3O_3VO_4$: (a) photo of bulk sample under optical microscope, (b) grain, SEM image.

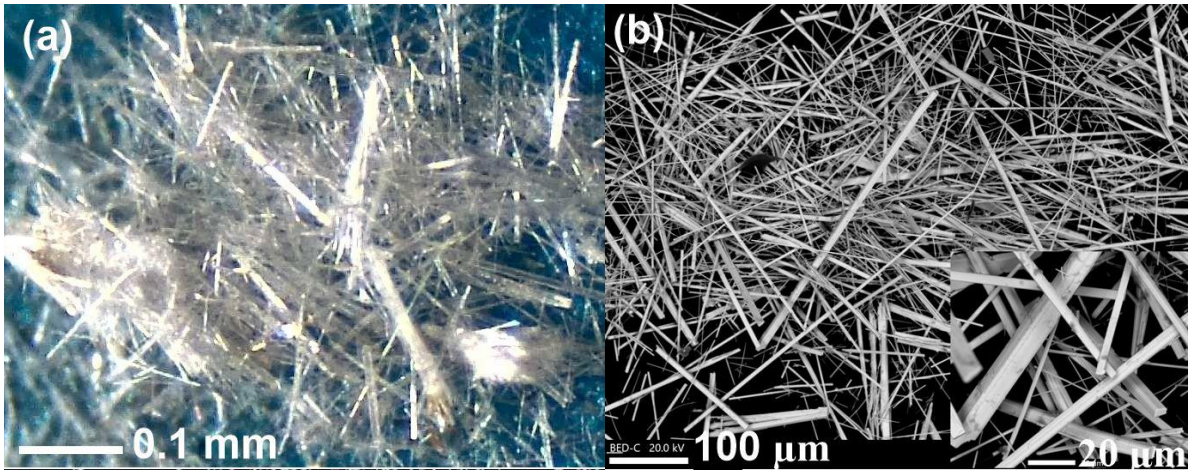

Figure S2. Needle-like crystals of $KBi_5O_5(PO_4)_2$: (a) photo under optical microscope, (b) SEM image.

2. Chemical composition

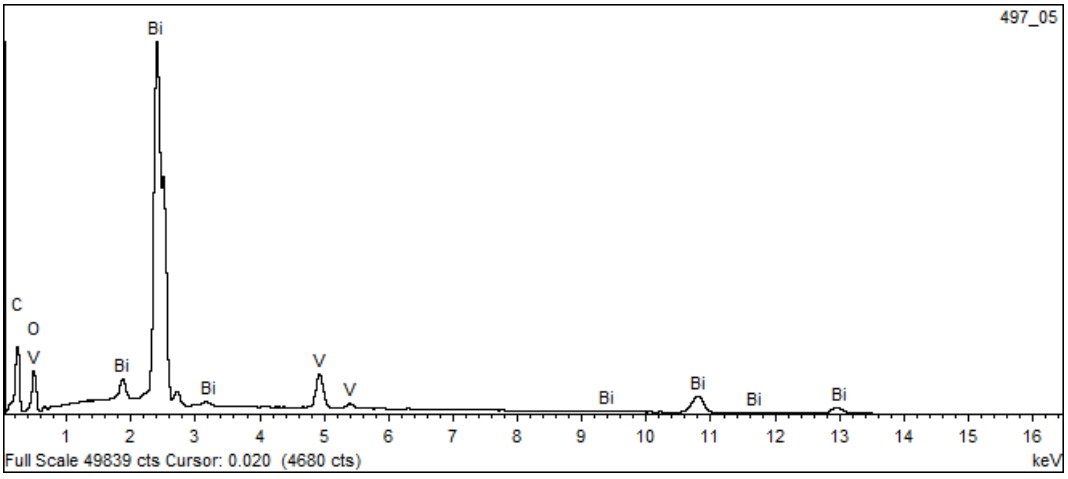

Figure S3. EDS spectrum of $Bi_3(VO_4)O_3$ compound.

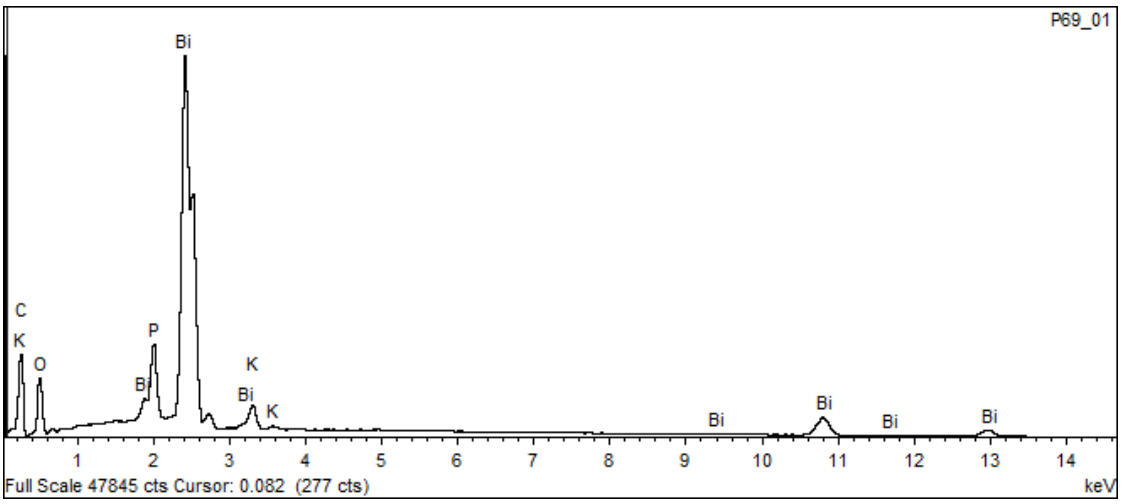

Figure S4. EDS spectrum of $KBi_5O_5(PO_4)_2$ compound.

Table S1. Chemical composition of sample (I)* determined by EDS analysis

	Atomic %			Weight %		
Element	Bi	V	O	Bi_2O_3	V_2O_5	Total
Point 1	27.23	9.12	63.65	89.53	11.71	101.24
Point 2	27.34	9.04	63.62	88.51	11.42	99.93
Point 3	27.23	9.12	63.65	88.58	11.58	100.16
Average value	27.26	9.09	63.64			

*Chemical formula. calculated from EDS results: $Bi_{2.99}V_{1.00}O_{7.00}$

Table S2. Chemical composition of sample (II)* determined by EDS analysis

	Atomic %				Weight %			
Element	K	Bi	P	O	K_2O	Bi_2O_3	P_2O_5	Total
Point 1	4.77	24.54	9.00	61.69	3.41	86.74	9.69	99.85
Point 2	4.82	24.56	8.96	61.66	3.42	86.17	9.58	99.17
Point 3	4.95	24.74	8.78	61.53	3.48	86.03	9.3	98.82
Average value	4.86	24.61	8.91	61.63				

*Chemical formula. calculated from EDS results: $K_{0.99}Bi_{4.99}P_{1.81}O_{12.52}$

The lower oxygen amount from the EDS analysis may be related to the small thickness of needle crystals. which is smaller than the size of the effective emission region of characteristic radiation for O. at 20 kV > 10-15 μm.

3. Thermal behavior

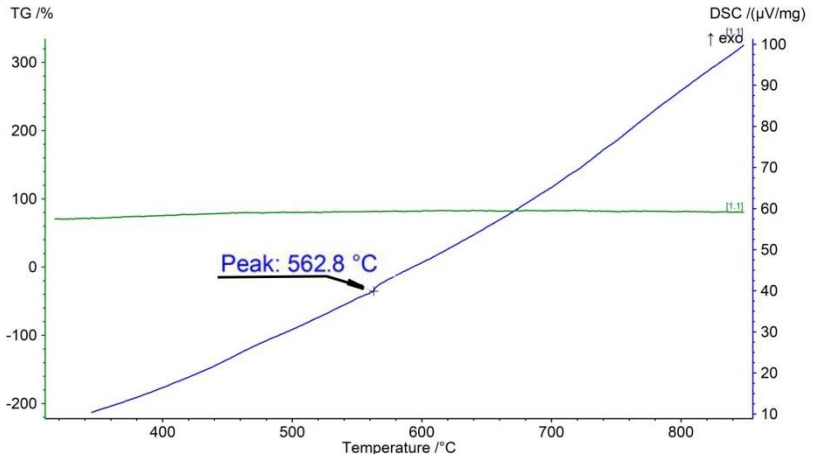

Figure S9. Thermogravimetric curves of β-$Bi_3O_3(VO_4)$.

4. X-ray diffraction data

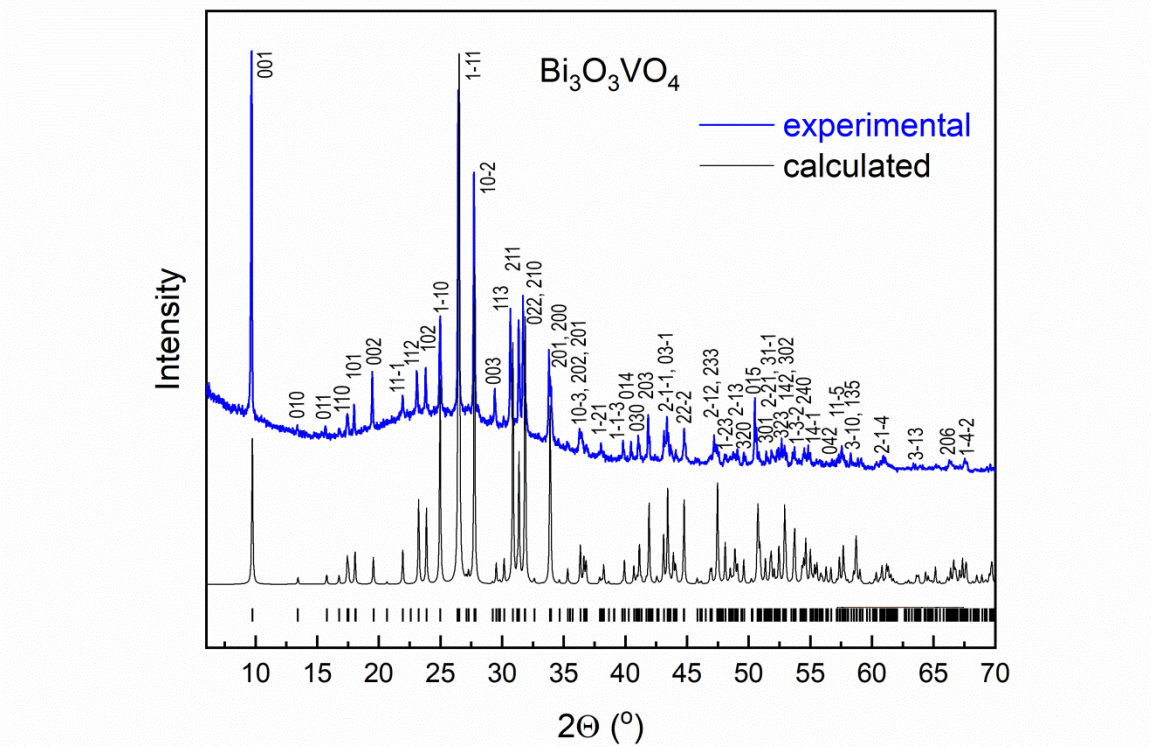

Figure S5. Experimental and calculated powder XRD patterns of β-$Bi_3O_3VO_4$ (the vertical ticks indicate the Bragg positions).

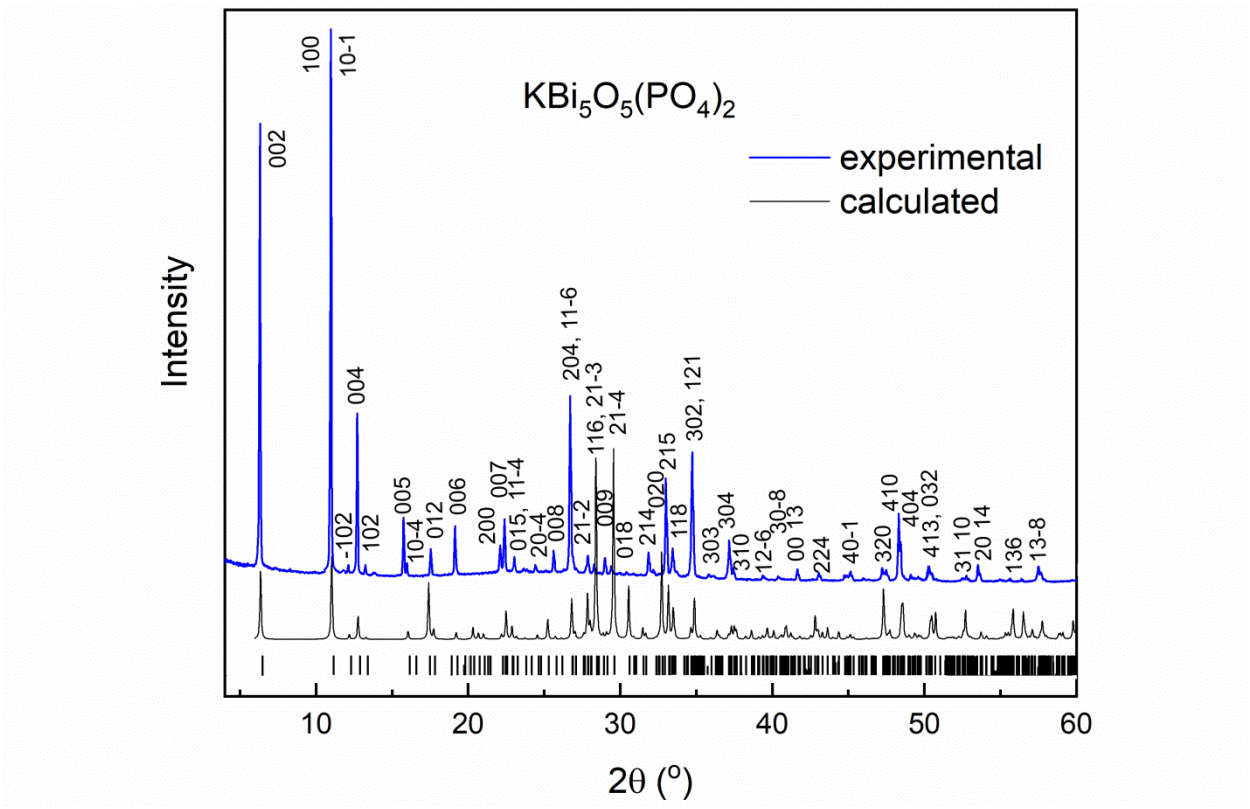

Figure S6. Experimental and calculated powder XRD patterns of $KBi_5O_5(PO_4)_2$ (the vertical ticks indicate the Bragg positions). The differences observed in the intensities of some Bragg peaks can be explained by the preferred orientation of the needle-like crystals.

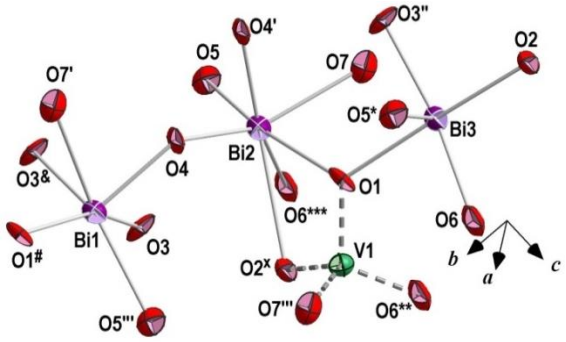

Figure S7. The basic structural units forming the crystal structure of β-$Bi_3O_3(VO_4)$ with atom-labelling scheme. Displacement ellipsoids are presented at the 80% probability level. [Symmetry codes: (') -x. 1-y. 1-z; (") x. -1+y. z; ('") 1+x. y. z; (*) 1+x. -1+y. z; (**) 1-x. -y. 2-z; (***) -1+x. 1+y. z; ($^{\&}$) -x. 2-y. 1-z; ($^{\#}$) 1-x. 1-y. 1-z; (^{x}) x. 1+y. z].

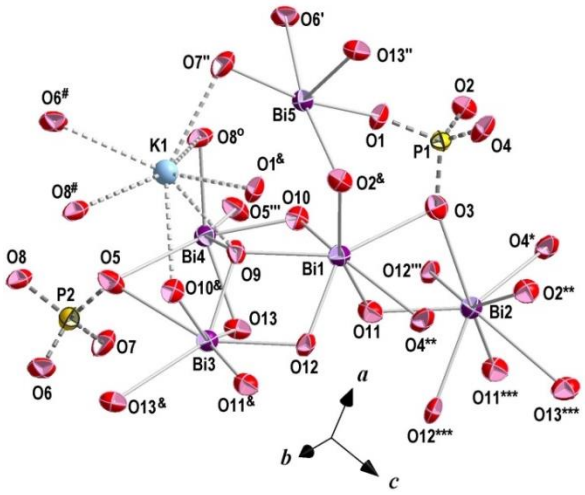

Figure S8. The basic structural units forming the crystal structure of $KBi_5O_5(PO_4)_2$ with atom-labelling scheme. Displacement ellipsoids are presented at the 80% probability level. [Symmetry codes: (') 1+x. -1+y. z; ('') 1+x. y. z; (''') x. -1+y. z; (*) 2-x. y. ½-z; (**) 2-x. ½+y. ½-z; (***) 1-x. -½+y. ½-z; ($^{\&}$) x. 1+y. z; ($^{\#}$) 1-x. 2-y. -z; (°) 1-x. 1-y. -z].

Table S3. Bond valence data for β-$Bi_3O_3(VO_4)$ (I)

	Bi1	**Bi2**	**Bi3**	**V1**	**Σ**
O1	0.168	0.236	0.475	1.205	2.08
O2		0.163	0.556	1.325	2.04
O3	0.684	0.097	0.646		2.03
	0.603				
O4	0.724	0.666			1.91
		0.518			
O5	0.391	0.646	0.771		1.92
	0.109				
O6		0.175	0.407	1.328	1.97
			0.060		
O7	0.236	0.420		1.238	1.89
Σ	2.92	2.92	2.92	5.10	

Table S4. Bond valence data for $KBi_5O_5(PO_4)_2$ (II)

	Bi1	**Bi2**	**Bi3**	**Bi4**	**Bi5**	**K**	**P1**	**P2**	**Σ**
O1					0.541		1.218		1.76
O2	0.171	0.140			0.413		1.241		1.97
O3	0.216	0.317					1.231		1.76
O4	0.240	0.357					1.148		1.75
O5			0.243	0.197				1.211	1.79
				0.138					
O6					0.551	0.152		1.251	1.95
O7					0.492	0.162		1.357	2.01
O8				0.462		0.152		1.265	2.03
						0.146			
O9	0.467		0.666	0.753		0.164			2.05
O10	0.552		0.659	0.733		0.155			2.10
O11	0.640	0.520	0.477						2.15
		0.510							

O12	0.593	0.669	0.592						2.18
		0.324							
O13		0.138	0.145	0.563	0.903				1.88
			0.126						
Σ	2.88	2.98	2.91	2.85	2.90	0.93	4.84	5.08	

Table S5. Selected geometric parameters (Å) for β-$Bi_3O_3(VO_4)$

Bi1—O4	2.145 (9)	Bi2—$O2^{vii}$	2.861 (9)
Bi1—O3	2.172 (8)	Bi2—O3	3.110 (9)
Bi1—$O3^{i}$	2.233 (9)	Bi3—$O5^{iv}$	2.115 (8)
Bi1—$O5^{ii}$	2.441 (9)	Bi3—$O3^{v}$	2.200 (9)
Bi1—$O7^{iii}$	2.683 (9)	Bi3—O2	2.272 (9)
Bi1—$O1^{viii}$	2.845 (9)	Bi3—O1	2.347 (9)
Bi1—$O5^{i}$	3.055 (9)	Bi3—O6	2.421 (9)
Bi2—$O4^{iii}$	2.185 (8)	Bi3—O6	3.344 (9)
Bi2—O5	2.200 (9)	V1—$O6^{vi}$	1.698 (10)
Bi2—O4	2.306 (8)	V1—$O2^{vii}$	1.699 (9)
Bi2—O7	2.406 (10)	V1—$O7^{ii}$	1.724 (10)
Bi2—O1	2.684 (9)	V1—O1	1.734 (9)
Bi2—$O6^{ix}$	2.827 (9)		

Symmetry code(s): (i) -*x*. -*y*+2. -*z*+1; (ii) *x*+1. *y*. *z*; (iii) -*x*. -*y*+1. -*z*+1; (iv) *x*+1. *y*-1. *z*; (v) *x*. *y*-1. *z*; (vi) -*x*+1. -*y*. -*z*+2; (vii) *x*. *y*+1. *z*; (viii) 1-*x*. 1-*y*. 1-*z*; (ix) -1+*x*. 1+*y*. *z*

Table S6. Selected geometric parameters (Å) for $KBi_5O_5(PO_4)_2$

Bi1—O11	2.204 (8)	Bi4—$O5^{ii}$	2.769 (8)
Bi1—O12	2.241 (8)	Bi5—$O13^{viii}$	2.039 (8)
Bi1—O10	2.275 (8)	Bi5—$O6^{ix}$	2.276 (8)
Bi1—O9	2.355 (8)	Bi5—O1	2.285 (8)
Bi1—$O4^{i}$	2.675 (8)	Bi5—$O7^{viii}$	2.330 (8)
Bi1—O3	2.725 (8)	Bi5—$O2^{v}$	2.415 (8)
Bi2—$O12^{ii}$	2.183 (8)	K1—O9	2.802 (8)
Bi2—$O11^{iii}$	2.304 (8)	K1—$O7^{viii}$	2.805 (9)
Bi2—O11	2.313 (9)	K1—$O10^{v}$	2.821 (8)
Bi2—$O4^{iv}$	2.484 (8)	K1—$O6^{x}$	2.829 (9)
Bi2—$O12^{iii}$	2.531 (8)	K1—$O8^{x}$	2.830 (8)
Bi2—O3	2.542 (8)	K1—$O8^{vi}$	2.843 (8)
Bi3—O9	2.185 (8)	P1—O2	1.537 (8)
Bi3—$O10^{v}$	2.190 (8)	P1—O3	1.540 (8)

Bi3—O12	2.242 (8)	P1—O1	1.544 (8)
Bi3—O11^{v}	2.345 (9)	P1—O4	1.566 (9)
Bi3—O5	2.668 (8)	P2—O7	1.504 (9)
Bi4—O9	2.126 (8)	P2—O8	1.530 (8)
Bi4—O10	2.139 (8)	P2—O6	1.534 (8)
Bi4—O13	2.263 (8)	P2—O5	1.546 (8)
Bi4—O8^{vi}	2.360 (7)		

Symmetry code(s): (i) -*x*+2. *y*+1/2. -*z*+1/2; (ii) *x*. *y*-1. *z*; (iii) -*x*+1. *y*-1/2. -*z*+1/2; (iv) -*x*+2. *y*-1/2. -*z*+1/2; (v) *x*. *y*+1. *z*; (vi) -*x*+1. -*y*+1. -*z*; (vii) *x*-1. *y*. *z*; (viii) *x*+1. *y*. *z*; (ix) *x*+1. *y*-1. *z*; (x) -*x*+1. -*y*+2. -*z*.

Table S7. Crystallographic parameters of structurally related oxosalts

	$KBi_5O_5(PO_4)_2$ (our work)	α-$Bi_3O_3(VO_4)$ (Colmont et al.. 2020)
Sp.group	$P2_1/c$	$P\bar{1}$
a. *b*. *c* (Å)	8.026(6). 5.462(4). 27.769(2)	5.682(1). 8.479(2). 14.243(3)
α. β. γ (°)	90.0. 95.7(2). 90.0	81.39(1). 86.91(1). 88.53(1)
V (Å^3)	1211.29(16)	677.389