

# Supporting Information

## Synthesis, Structure and Properties of Two New Selenite Optical

### Materials: $\text{K}_2\text{Zn}_3\text{Se}_4\text{O}_{12}$ , $\text{K}_4\text{Zn}_3\text{V}_4\text{Se}_2\text{O}_{19}$

*Qiuyuan Feng,<sup>a</sup> Zhixia Gao,<sup>a</sup> Ketian Hou,<sup>b</sup> Jialong Wang,<sup>b</sup> Hong Du<sup>\*a</sup> and Qun Jing<sup>\*b</sup>*

*<sup>a</sup>College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi, Xinjiang 830054, P. R. China.*

*<sup>b</sup>School of Physical Science and Technology, Xinjiang University, Urumqi, Xinjiang 830017, China.*

\*E-mails: 175790509@qq.com (Hong Du); qunjing@xju.edu.cn (Qun Jing);

## Content

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**Table S1.** Atomic coordinates and equivalent isotropic displacement parameters and bond valence sum (BVS) calculations for  $\text{K}_2\text{Zn}_3\text{Se}_4\text{O}_{12}$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table S2.** The selected bond lengths and angles of  $\text{K}_2\text{Zn}_3\text{Se}_4\text{O}_{12}$ .

**Table S3.** Atomic coordinates and equivalent isotropic displacement parameters and bond valence sum (BVS) calculations for  $\text{K}_4\text{Zn}_3\text{V}_4\text{Se}_2\text{O}_{19}$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table S4.** The selected bond lengths and angles of  $\text{K}_4\text{Zn}_3\text{V}_4\text{Se}_2\text{O}_{19}$ .

**Table S5.** Vanadate-selenite. Note the following compounds are all from ICSD and the anionic group is the  $[\text{VSeO}_x]$  group, except for other disordered structures, fluorides, and structures containing crystalline water, all vanadate-selenite are summarized.

**Figure S1.** (a) Energy dispersive X-ray spectroscopy (EDS) analysis for  $\text{K}_2\text{Zn}_3\text{Se}_4\text{O}_{12}$ .

(b) Energy dispersive X-ray spectroscopy (EDS) analysis for  $\text{K}_4\text{Zn}_3\text{V}_4\text{Se}_2\text{O}_{19}$ .

**Table S1.** Atomic coordinates and equivalent isotropic displacement parameters and bond valence sum (BVS)\* calculations for  $K_2Zn_3Se_4O_{12}$ .  $U(eq)$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

| Atoms | x/a     | y/b      | z/c     | U(eq) | BVS   |
|-------|---------|----------|---------|-------|-------|
| K(1)  | -14(1)  | 11252(2) | 1641(1) | 29(1) | 1.040 |
| K(2)  | 5057(1) | 6640(2)  | 3289(1) | 29(1) | 0.960 |
| Zn(1) | 2595(1) | 8922(1)  | 2682(1) | 20(1) | 1.971 |
| Zn(2) | 6141(1) | 11278(1) | 4214(1) | 21(1) | 2.003 |
| Zn(3) | 1027(1) | 6622(1)  | 752(1)  | 22(1) | 1.969 |
| Se(1) | 1191(1) | 11113(1) | 4023(1) | 19(1) | 4.300 |
| Se(2) | 6165(1) | 6746(1)  | 933(1)  | 16(1) | 4.213 |
| Se(3) | 2458(1) | 4459(1)  | 2254(1) | 19(1) | 4.242 |
| Se(4) | 7466(1) | 5019(1)  | 4477(1) | 20(1) | 4.218 |
| O(1)  | 5928(4) | 6223(7)  | -198(3) | 24(1) | 2.105 |
| O(2)  | 6870(4) | 5113(8)  | 3396(3) | 27(1) | 2.049 |
| O(3)  | 1476(4) | 10463(9) | 2966(3) | 32(1) | 2.142 |
| O(4)  | 5089(3) | 7581(8)  | 1221(4) | 27(1) | 2.068 |
| O(5)  | 1787(4) | 4376(8)  | 1225(4) | 31(1) | 1.964 |
| O(6)  | 738(4)  | 9067(7)  | 4434(3) | 25(1) | 2.186 |
| O(7)  | 6255(4) | 4543(7)  | 1447(4) | 26(1) | 2.037 |
| O(8)  | 3533(4) | 5372(10) | 2025(4) | 35(1) | 2.088 |
| O(9)  | 172(4)  | 12336(8) | 3683(4) | 32(1) | 2.170 |
| O(10) | 7018(5) | 2996(10) | 4913(4) | 47(2) | 2.169 |
| O(11) | 1974(4) | 6395(8)  | 2752(4) | 36(1) | 2.020 |
| O(12) | 8584(4) | 4340(8)  | 4257(4) | 34(1) | 2.017 |

(BVS)\*: The bond valence sums were calculated using the formula  $V_i = \sum S_{ij} = \sum \exp[(r_0 - r_{ij})/B]$ , where  $S_{ij}$  is the bond valence associated with bond length  $r_{ij}$ , and  $r_0$  and  $B$  (usually 0.37) are empirically determined parameters.<sup>1</sup>

**Table S2.** The selected bond lengths and angles of  $K_2Zn_3Se_4O_{12}$ .

|                      |            |                      |            |
|----------------------|------------|----------------------|------------|
| K(1)-O(6)#1          | 2.627(5)   | Zn(2)-O(1)#6         | 1.959(5)   |
| K(1)-O(3)            | 2.735(5)   | Zn(2)-O(4)#3         | 1.980(5)   |
| K(1)-O(9)#2          | 2.749(6)   | Zn(2)-O(8)#3         | 1.989(5)   |
| K(1)-O(12)#3         | 2.804(6)   | Zn(3)-O(12)#3        | 1.954(6)   |
| K(1)-O(11)#1         | 2.941(6)   | Zn(3)-O(5)           | 1.961(5)   |
| K(1)-O(9)            | 3.031(6)   | Zn(3)-O(6)#8         | 1.966(5)   |
| K(1)-O(5)#4          | 3.400(6)   | Zn(3)-O(9)#2         | 1.985(5)   |
| K(2)-O(2)            | 2.720(5)   | Se(1)-O(3)           | 1.675(5)   |
| K(2)-O(7)#3          | 2.760(5)   | Se(1)-O(6)           | 1.678(5)   |
| K(2)-O(8)            | 2.799(6)   | Se(1)-O(9)           | 1.680(5)   |
| K(2)-O(1)#6          | 2.812(5)   | Se(2)-O(1)           | 1.676(5)   |
| K(2)-O(4)#7          | 2.903(5)   | Se(2)-O(4)           | 1.690(5)   |
| K(2)-O(4)            | 3.062(6)   | Se(2)-O(7)           | 1.691(5)   |
| K(2)-O(8)#3          | 3.293(7)   | Se(3)-O(5)           | 1.678(5)   |
| Zn(1)-O(11)          | 1.952(6)   | Se(3)-O(8)           | 1.682(5)   |
| Zn(1)-O(3)           | 1.959(5)   | Se(3)-O(11)          | 1.688(6)   |
| Zn(1)-O(2)#3         | 1.969(5)   | Se(4)-O(10)          | 1.675(6)   |
| Zn(1)-O(7)#3         | 1.983(5)   | Se(4)-O(12)          | 1.681(5)   |
| Zn(2)-O(10)#4        | 1.917(6)   | Se(4)-O(2)           | 1.698(5)   |
| Zn(2)-O(1)#8         | 1.959(5)   | K(2)-O(7)#7          | 2.760(5)   |
| K(2)-O(1)#8          | 2.812(5)   | Zn(2)-O(8)#7         | 1.989(5)   |
| Zn(1)-O(2)#7         | 1.969(5)   | K(2)-O(8)#7          | 3.293(7)   |
| Zn(2)-O(4)#7         | 1.980(5)   | Zn(3)-O(9)#1         | 1.985(5)   |
| K(2)-O(4)#3          | 2.903(5)   | K(1)-O(9)#1          | 2.749(6)   |
| K(1)-O(5)#9          | 3.400(6)   | Zn(2)-O(10)#9        | 1.917(6)   |
| Zn(3)-O(6)#6         | 1.966(5)   | K(1)-O(11)#2         | 2.941(6)   |
| K(1)-O(6)#2          | 2.627(5)   | Zn(3)-O(12)#7        | 1.954(6)   |
| Zn(1)-O(7)#7         | 1.983(5)   | K(1)-O(12)#7         | 2.804(6)   |
| O(6)#1-K(1)-O(3)     | 141.45(19) | O(2)-K(2)-O(8)#3     | 75.63(16)  |
| O(6)#1-K(1)-O(9)#2   | 127.37(18) | O(7)#3-K(2)-O(8)#3   | 81.95(15)  |
| O(3)-K(1)-O(9)#2     | 88.06(19)  | O(8)-K(2)-O(8)#3     | 125.24(14) |
| O(6)#1-K(1)-O(12)#3  | 108.82(18) | O(1)#6-K(2)-O(8)#3   | 58.65(14)  |
| O(3)-K(1)-O(12)#3    | 73.05(17)  | O(4)#7-K(2)-O(8)#3   | 147.71(14) |
| O(9)#2-K(1)-O(12)#3  | 60.45(16)  | O(4)-K(2)-O(8)#3     | 68.59(13)  |
| O(6)#1-K(1)-O(11)#1  | 80.71(16)  | O(11)-Zn(1)-O(3)     | 96.4(3)    |
| O(3)-K(1)-O(11)#1    | 117.23(17) | O(11)-Zn(1)-O(2)#3   | 128.0(2)   |
| O(9)#2-K(1)-O(11)#1  | 91.32(16)  | O(3)-Zn(1)-O(2)#3    | 107.8(2)   |
| O(12)#3-K(1)-O(11)#1 | 150.56(18) | O(11)-Zn(1)-O(7)#3   | 119.6(2)   |
| O(6)#1-K(1)-O(9)     | 112.64(15) | O(3)-Zn(1)-O(7)#3    | 110.9(2)   |
| O(3)-K(1)-O(9)       | 51.66(14)  | O(2)#3-Zn(1)-O(7)#3  | 94.0(2)    |
| O(9)#2-K(1)-O(9)     | 114.00(17) | O(10)#4-Zn(2)-O(1)#6 | 115.6(2)   |
| O(12)#3-K(1)-O(9)    | 124.65(17) | O(10)#4-Zn(2)-O(4)#3 | 111.8(3)   |
| O(11)#1-K(1)-O(9)    | 72.31(17)  | O(1)#6-Zn(2)-O(4)#3  | 112.1(2)   |

|                     |            |                      |          |
|---------------------|------------|----------------------|----------|
| O(6)#1-K(1)-O(5)#4  | 70.88(15)  | O(10)#4-Zn(2)-O(8)#3 | 118.7(3) |
| O(3)-K(1)-O(5)#4    | 74.35(16)  | O(1)#6-Zn(2)-O(8)#3  | 99.8(2)  |
| O(9)#2-K(1)-O(5)#4  | 129.93(15) | O(4)#3-Zn(2)-O(8)#3  | 96.9(2)  |
| O(12)#3-K(1)-O(5)#4 | 69.58(15)  | O(12)#3-Zn(3)-O(5)   | 128.4(2) |
| O(11)#1-K(1)-O(5)#4 | 138.51(15) | O(12)#3-Zn(3)-O(6)#8 | 104.9(2) |
| O(9)-K(1)-O(5)#4    | 91.15(14)  | O(5)-Zn(3)-O(6)#8    | 101.5(2) |
| O(2)-K(2)-O(7)#3    | 153.30(17) | O(12)#3-Zn(3)-O(9)#2 | 90.4(2)  |
| O(2)-K(2)-O(8)      | 123.60(18) | O(5)-Zn(3)-O(9)#2    | 119.9(3) |
| O(7)#3-K(2)-O(8)    | 81.36(17)  | O(6)#8-Zn(3)-O(9)#2  | 110.9(2) |
| O(2)-K(2)-O(1)#6    | 80.36(16)  | O(3)-Se(1)-O(6)      | 103.1(3) |
| O(7)#3-K(2)-O(1)#6  | 75.63(15)  | O(3)-Se(1)-O(9)      | 97.7(3)  |
| O(8)-K(2)-O(1)#6    | 155.89(18) | O(6)-Se(1)-O(9)      | 101.1(3) |
| O(2)-K(2)-O(4)#7    | 72.42(15)  | O(1)-Se(2)-O(4)      | 102.6(3) |
| O(7)#3-K(2)-O(4)#7  | 127.23(16) | O(1)-Se(2)-O(7)      | 103.5(2) |
| O(8)-K(2)-O(4)#7    | 77.92(17)  | O(4)-Se(2)-O(7)      | 103.2(3) |
| O(1)#6-K(2)-O(4)#7  | 110.60(15) | O(5)-Se(3)-O(8)      | 105.5(3) |
| O(2)-K(2)-O(4)      | 92.15(15)  | O(5)-Se(3)-O(11)     | 101.2(3) |
| O(7)#3-K(2)-O(4)    | 93.02(15)  | O(8)-Se(3)-O(11)     | 100.6(3) |
| O(8)-K(2)-O(4)      | 60.72(15)  | O(10)-Se(4)-O(12)    | 102.8(3) |
| O(1)#6-K(2)-O(4)    | 126.99(15) | O(10)-Se(4)-O(2)     | 102.2(3) |
| O(4)#7-K(2)-O(4)    | 116.79(16) | O(12)-Se(4)-O(2)     | 102.4(3) |

Symmetry transformations used to generate equivalent atoms:

|                      |                      |               |
|----------------------|----------------------|---------------|
| #1 -x,y+1/2,-z+1/2   | #2 -x,y-1/2,-z+1/2   |               |
| #3 -x+1,y+1/2,-z+1/2 | #4 x,y+1,z           | #5 -x,-y+2,-z |
| #6 x,-y+3/2,z+1/2    | #7 -x+1,y-1/2,-z+1/2 |               |
| #8 x,-y+3/2,z-1/2    | #9 x,y-1,z           |               |

**Table S3.** Atomic coordinates and equivalent isotropic displacement parameters and bond valence sum (BVS)\* calculations for  $K_4Zn_3V_4Se_2O_{19}$ .  $U(eq)$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

| Atoms | x/a     | y/b      | z/c     | U(eq) | BVS   |
|-------|---------|----------|---------|-------|-------|
| K(1)  | 4293(1) | 6748(1)  | 4197(1) | 22(1) | 1.151 |
| K(2)  | 2736(1) | 13152(2) | 2775(1) | 31(1) | 1.055 |
| Zn(1) | 9149(1) | 5339(1)  | 6580(1) | 17(1) | 1.975 |
| Zn(2) | 5000    | 3349(1)  | 2500    | 19(1) | 1.970 |
| V(4)  | 6120(1) | 5886(1)  | 3807(1) | 17(1) | 5.082 |
| V(1A) | 7562(1) | 4033(3)  | 5262(2) | 17(1) | 5.056 |
| V(1B) | 7624(1) | 4643(2)  | 4937(2) | 16(1) | 4.806 |
| Se(1) | 4387(1) | 10923(1) | 3896(1) | 16(1) | 4.046 |
| O(1)  | 5310(2) | 11127(4) | 4165(3) | 21(1) | 1.980 |
| O(2)  | 5818(2) | 7633(4)  | 4034(3) | 26(1) | 2.103 |
| O(3)  | 4335(2) | 9371(4)  | 3107(3) | 23(1) | 1.988 |
| O(4)  | 4167(2) | 12322(4) | 2986(3) | 24(1) | 2.046 |
| O(5)  | 5388(2) | 4712(4)  | 3666(3) | 27(1) | 1.882 |
| O(6)  | 6747(2) | 5173(4)  | 4977(3) | 26(1) | 2.032 |
| O(7)  | 8099(2) | 4753(5)  | 6229(3) | 26(1) | 1.742 |
| O(8)  | 6534(2) | 5856(5)  | 2754(3) | 32(1) | 1.910 |
| O(9A) | 7745(5) | 2828(11) | 4346(8) | 0(2)  | 1.850 |
| O(9B) | 7952(4) | 5834(9)  | 4178(7) | 30(2) | 1.893 |
| O(9C) | 7978(5) | 3799(11) | 4242(8) | 0(2)  | 1.886 |

(BVS)\*: The bond valence sums were calculated using the formula  $V_i = \sum S_{ij} = \sum \exp[(r_0 - r_{ij})/B]$ , where  $S_{ij}$  is the bond valence associated with bond length  $r_{ij}$ , and  $r_0$  and  $B$  (usually 0.37) are empirically determined parameters.<sup>1</sup>

**Table S4.** The selected bond lengths and angles of  $K_4Zn_3V_4Se_2O_{19}$ .

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|               |           |                |           |
|---------------|-----------|----------------|-----------|
| K(1)-O(3)     | 2.708(4)  | V(1A)-O(9A)    | 1.651(10) |
| K(1)-O(1)#1   | 2.825(4)  | V(1A)-O(6)     | 1.807(4)  |
| K(1)-O(8)#2   | 2.838(4)  | V(1A)-O(9A)#12 | 1.831(11) |
| K(1)-O(5)     | 2.865(4)  | V(1A)-O(9B)    | 2.293(8)  |
| K(1)-O(6)#3   | 2.879(4)  | V(1B)-O(9C)    | 1.394(10) |
| K(1)-O(2)     | 2.968(4)  | V(1B)-O(9B)    | 1.609(8)  |
| K(1)-O(5)#3   | 2.997(4)  | V(1B)-O(6)     | 1.698(4)  |
| K(1)-O(9C)#4  | 3.041(10) | V(1B)-O(7)     | 1.755(4)  |
| K(1)-O(9A)#4  | 3.052(10) | V(1B)-O(9A)    | 1.799(10) |
| K(2)-O(9B)#4  | 2.710(8)  | Se(1)-O(3)     | 1.695(4)  |
| K(2)-O(4)     | 2.723(4)  | Se(1)-O(1)     | 1.703(3)  |
| K(2)-O(9A)#5  | 2.740(10) | Se(1)-O(4)     | 1.704(4)  |
| K(2)-O(9C)#5  | 2.778(10) | Zn(1)-O(1)#8   | 1.965(4)  |
| K(2)-O(7)#1   | 2.830(4)  | K(1)-O(1)#1    | 2.825(4)  |
| K(2)-O(8)#5   | 2.872(4)  | Zn(1)-O(2)#8   | 1.958(4)  |
| K(2)-O(8)#4   | 3.008(5)  | Zn(1)-O(3)#6   | 1.947(4)  |
| K(2)-O(6)#1   | 3.245(4)  | Zn(2)-O(4)#13  | 1.966(4)  |
| K(2)-O(7)#6   | 3.363(4)  | K(1)-O(5)#3    | 2.997(4)  |
| Zn(1)-O(3)#7  | 1.947(4)  | K(1)-O(6)#3    | 2.879(4)  |
| Zn(1)-O(2)#8  | 1.958(4)  | K(2)-O(6)#1    | 3.245(4)  |
| Zn(1)-O(1)#8  | 1.965(4)  | K(2)-O(7)#1    | 2.830(4)  |
| Zn(1)-O(7)    | 1.997(4)  | K(2)-O(7)#7    | 3.363(4)  |
| Zn(2)-O(5)    | 1.966(4)  | K(1)-O(8)#2    | 2.838(4)  |
| Zn(2)-O(5)#2  | 1.966(4)  | K(2)-O(8)#10   | 2.872(4)  |
| Zn(2)-O(4)#9  | 1.966(4)  | K(2)-O(8)#11   | 3.008(5)  |
| Zn(2)-O(4)#10 | 1.966(4)  | V(1A)-O(9A)#12 | 1.831(11) |
| V(4)-O(8)     | 1.643(4)  | K(2)-O(9A)#10  | 2.740(10) |
| V(4)-O(2)     | 1.680(4)  | K(1)-O(9A)#11  | 3.052(10) |
| V(4)-O(5)     | 1.695(4)  | K(2)-O(9B)#11  | 2.710(8)  |

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|                     |            |                      |            |
|---------------------|------------|----------------------|------------|
| V(4)-O(6)           | 1.862(4)   | K(2)-O(9C)#10        | 2.778(10)  |
| V(1A)-O(7)          | 1.599(4)   | K(1)-O(9C)#11        | 3.041(10)  |
| V(1A)-O(9C)         | 1.620(10)  | O(9A)#5-K(2)-O(6)#1  | 158.9(2)   |
| O(3)-K(1)-O(1)#1    | 77.85(11)  | O(9C)#5-K(2)-O(6)#1  | 139.9(2)   |
| O(3)-K(1)-O(8)#2    | 80.69(12)  | O(7)#1-K(2)-O(6)#1   | 54.18(10)  |
| O(1)#1-K(1)-O(8)#2  | 151.97(12) | O(8)#5-K(2)-O(6)#1   | 75.04(11)  |
| O(3)-K(1)-O(5)      | 109.83(12) | O(8)#4-K(2)-O(6)#1   | 115.89(11) |
| O(1)#1-K(1)-O(5)    | 118.37(11) | O(9B)#4-K(2)-O(7)#6  | 77.9(2)    |
| O(8)#2-K(1)-O(5)    | 85.83(12)  | O(4)-K(2)-O(7)#6     | 65.01(11)  |
| O(3)-K(1)-O(6)#3    | 139.73(12) | O(9A)#5-K(2)-O(7)#6  | 53.4(2)    |
| O(1)#1-K(1)-O(6)#3  | 103.59(12) | O(9C)#5-K(2)-O(7)#6  | 73.8(2)    |
| O(8)#2-K(1)-O(6)#3  | 81.66(12)  | O(7)#1-K(2)-O(7)#6   | 158.66(7)  |
| O(5)-K(1)-O(6)#3    | 104.61(12) | O(8)#5-K(2)-O(7)#6   | 110.69(12) |
| O(3)-K(1)-O(2)      | 68.85(11)  | O(8)#4-K(2)-O(7)#6   | 72.12(11)  |
| O(1)#1-K(1)-O(2)    | 74.33(11)  | O(6)#1-K(2)-O(7)#6   | 143.89(10) |
| O(8)#2-K(1)-O(2)    | 114.06(12) | O(3)#7-Zn(1)-O(2)#8  | 105.63(15) |
| O(5)-K(1)-O(2)      | 55.54(11)  | O(3)#7-Zn(1)-O(1)#8  | 122.91(16) |
| O(6)#3-K(1)-O(2)    | 151.08(11) | O(2)#8-Zn(1)-O(1)#8  | 111.08(16) |
| O(3)-K(1)-O(5)#3    | 144.96(11) | O(3)#7-Zn(1)-O(7)    | 106.41(17) |
| O(1)#1-K(1)-O(5)#3  | 67.40(11)  | O(2)#8-Zn(1)-O(7)    | 103.48(17) |
| O(8)#2-K(1)-O(5)#3  | 133.58(12) | O(1)#8-Zn(1)-O(7)    | 105.65(16) |
| O(5)-K(1)-O(5)#3    | 83.94(12)  | O(5)-Zn(2)-O(5)#2    | 104.5(2)   |
| O(6)#3-K(1)-O(5)#3  | 57.76(11)  | O(5)-Zn(2)-O(4)#9    | 105.04(17) |
| O(2)-K(1)-O(5)#3    | 96.57(11)  | O(5)#2-Zn(2)-O(4)#9  | 107.71(16) |
| O(3)-K(1)-O(9C)#4   | 65.5(2)    | O(5)-Zn(2)-O(4)#10   | 107.71(16) |
| O(1)#1-K(1)-O(9C)#4 | 73.3(2)    | O(5)#2-Zn(2)-O(4)#10 | 105.04(17) |
| O(8)#2-K(1)-O(9C)#4 | 81.5(2)    | O(4)#9-Zn(2)-O(4)#10 | 125.2(2)   |
| O(5)-K(1)-O(9C)#4   | 167.0(2)   | O(8)-V(4)-O(2)       | 111.3(2)   |
| O(6)#3-K(1)-O(9C)#4 | 76.3(2)    | O(8)-V(4)-O(5)       | 111.4(2)   |

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|                      |            |                      |            |
|----------------------|------------|----------------------|------------|
| O(2)-K(1)-O(9C)#4    | 128.1(2)   | O(2)-V(4)-O(5)       | 107.4(2)   |
| O(5)#3-K(1)-O(9C)#4  | 106.9(2)   | O(8)-V(4)-O(6)       | 109.9(2)   |
| O(3)-K(1)-O(9A)#4    | 82.2(2)    | O(2)-V(4)-O(6)       | 110.81(19) |
| O(1)#1-K(1)-O(9A)#4  | 83.8(2)    | O(5)-V(4)-O(6)       | 105.88(19) |
| O(8)#2-K(1)-O(9A)#4  | 75.6(2)    | O(7)-V(1A)-O(9C)     | 110.9(4)   |
| O(5)-K(1)-O(9A)#4    | 156.1(2)   | O(7)-V(1A)-O(9A)     | 129.3(4)   |
| O(6)#3-K(1)-O(9A)#4  | 58.4(2)    | O(9C)-V(1A)-O(9A)    | 34.8(5)    |
| O(2)-K(1)-O(9A)#4    | 146.5(2)   | O(7)-V(1A)-O(6)      | 109.9(2)   |
| O(5)#3-K(1)-O(9A)#4  | 98.0(2)    | O(9C)-V(1A)-O(6)     | 113.0(4)   |
| O(9C)#4-K(1)-O(9A)#4 | 18.5(3)    | O(9A)-V(1A)-O(6)     | 117.9(4)   |
| O(9B)#4-K(2)-O(4)    | 71.63(18)  | O(7)-V(1A)-O(9A)#12  | 109.1(4)   |
| O(9B)#4-K(2)-O(9A)#5 | 124.7(3)   | O(9C)-V(1A)-O(9A)#12 | 108.0(5)   |
| O(4)-K(2)-O(9A)#5    | 103.9(2)   | O(9A)-V(1A)-O(9A)#12 | 73.8(5)    |
| O(9B)#4-K(2)-O(9C)#5 | 140.6(3)   | O(6)-V(1A)-O(9A)#12  | 105.7(3)   |
| O(4)-K(2)-O(9C)#5    | 118.1(2)   | O(7)-V(1A)-O(9B)     | 88.6(3)    |
| O(9A)#5-K(2)-O(9C)#5 | 20.4(3)    | O(9C)-V(1A)-O(9B)    | 51.3(4)    |
| O(9B)#4-K(2)-O(7)#1  | 103.5(2)   | O(9A)-V(1A)-O(9B)    | 84.5(4)    |
| O(4)-K(2)-O(7)#1     | 136.01(13) | O(6)-V(1A)-O(9B)     | 79.7(3)    |
| O(9A)#5-K(2)-O(7)#1  | 113.1(2)   | O(9A)#12-V(1A)-O(9B) | 157.6(4)   |
| O(9C)#5-K(2)-O(7)#1  | 93.7(2)    | O(9C)-V(1B)-O(9B)    | 73.1(5)    |
| O(9B)#4-K(2)-O(8)#5  | 138.93(19) | O(9C)-V(1B)-O(6)     | 135.1(5)   |
| O(4)-K(2)-O(8)#5     | 76.22(12)  | O(9B)-V(1B)-O(6)     | 106.6(3)   |
| O(9A)#5-K(2)-O(8)#5  | 87.1(2)    | O(9C)-V(1B)-O(7)     | 114.2(5)   |
| O(9C)#5-K(2)-O(8)#5  | 77.7(2)    | O(9B)-V(1B)-O(7)     | 110.4(3)   |
| O(7)#1-K(2)-O(8)#5   | 82.55(12)  | O(6)-V(1B)-O(7)      | 107.9(2)   |
| O(9B)#4-K(2)-O(8)#4  | 62.28(18)  | O(9C)-V(1B)-O(9A)    | 32.6(5)    |
| O(4)-K(2)-O(8)#4     | 121.87(12) | O(9B)-V(1B)-O(9A)    | 104.3(5)   |
| O(9A)#5-K(2)-O(8)#4  | 77.7(2)    | O(6)-V(1B)-O(9A)     | 115.9(4)   |
| O(9C)#5-K(2)-O(8)#4  | 83.1(2)    | O(7)-V(1B)-O(9A)     | 111.5(4)   |

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|                     |           |                 |            |
|---------------------|-----------|-----------------|------------|
| O(7)#1-K(2)-O(8)#4  | 89.50(11) | O(3)-Se(1)-O(1) | 99.93(18)  |
| O(8)#5-K(2)-O(8)#4  | 158.60(9) | O(3)-Se(1)-O(4) | 101.12(19) |
| O(9B)#4-K(2)-O(6)#1 | 76.3(2)   | O(1)-Se(1)-O(4) | 101.11(18) |
| O(4)-K(2)-O(6)#1    | 83.04(11) |                 |            |

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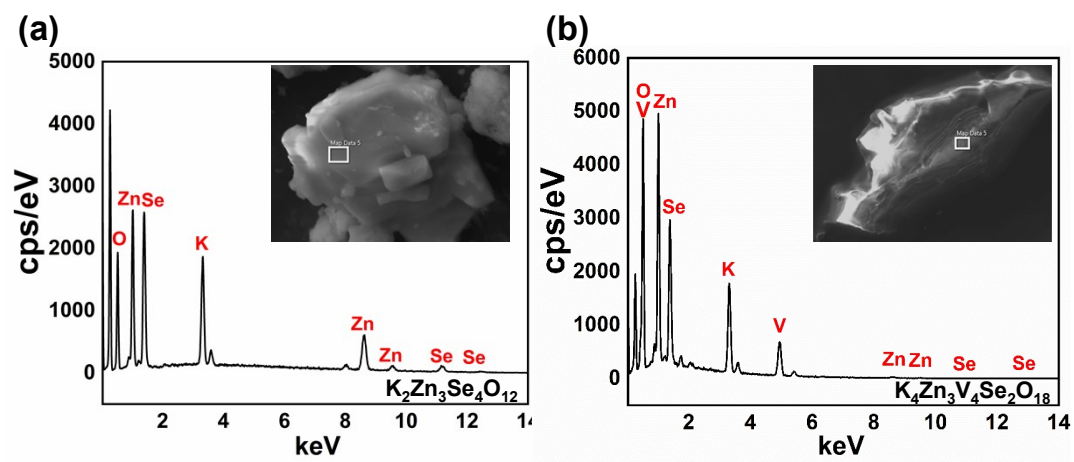
Symmetry transformations used to generate equivalent atoms:

|                           |                           |                            |
|---------------------------|---------------------------|----------------------------|
| #1 $-x+1, -y+2, -z+1$     | #2 $-x+1, y, -z+1/2$      | #3 $-x+1, -y+1, -z+1$      |
| #4 $x-1/2, y+1/2, z$      | #5 $-x+1, y+1, -z+1/2$    | #6 $x-1/2, -y+3/2, z-1/2$  |
| #7 $x+1/2, -y+3/2, z+1/2$ | #7 $x+1/2, -y+3/2, z+1/2$ | #9 $x, y-1, z$             |
| #10 $-x+1, y-1, -z+1/2$   | #11 $x+1/2, y-1/2, z$     | #12 $-x+3/2, -y+1/2, -z+1$ |
| #13 $x, y+1, z$           |                           |                            |

**Table S5.** Vanadate-selenite. Note the following compounds are all from ICSD and the anionic group is the [VSeO<sub>x</sub>] group, except for other disordered structures, fluorides, and structures containing crystalline water, all vanadate-selenite are summarized.

| No. | Compounds  | Dimension | Basic units                           | Space group                       | Ref. |
|-----|--|-----------|---------------------------------------|-----------------------------------|------|
| 1   | Cs(VSeO <sub>5</sub> )   | 0D        | [VO <sub>5</sub> ]                    | <i>P2</i> <sub>1</sub>            | 2    |
| 2   | V <sub>2</sub> (Se <sub>2</sub> O <sub>9</sub> )   | 0D        | [V <sub>4</sub> O <sub>18</sub> ]     | <i>P2</i> <sub>1</sub> / <i>c</i> | 3    |
| 3   | (VO) <sub>2</sub> (SeO <sub>3</sub> ) <sub>3</sub>   | 0D        | [VO <sub>5</sub> ]                    | <i>P2</i> <sub>1</sub> / <i>c</i> | 4    |
| 4   | Cu(VO)(SeO <sub>3</sub> ) <sub>2</sub>   | 0D        | [V <sub>2</sub> O <sub>10</sub> ]     | <i>P2</i> <sub>1</sub> / <i>c</i> | 5    |
| 5   | V <sub>2</sub> Se <sub>2</sub> O <sub>9</sub>  | 0D        | [VO <sub>5</sub> ]                    | <i>P2</i> <sub>1</sub> / <i>c</i> | 6    |
| 6   | Nd <sub>7</sub> VO <sub>4</sub> Se <sub>8</sub>  | 0D        | [VSe <sub>2</sub> O <sub>2</sub> ]    | Pbam                              | 7    |
| 7   | Sm <sub>7</sub> VO <sub>4</sub> Se <sub>8</sub>  | 0D        | [VSe <sub>2</sub> O <sub>2</sub> ]    | Pbam                              | 7    |
| 8   | V <sub>2</sub> O <sub>3</sub> (SeO <sub>4</sub> ) <sub>2</sub>   | 0D        | [V <sub>2</sub> O <sub>11</sub> ]     | <i>C2</i> / <i>c</i>              | 8    |
| 9   | Pb <sub>2</sub> V <sub>2</sub> Se <sub>2</sub> O <sub>11</sub>   | 0D        | [V <sub>4</sub> O <sub>16</sub> ]     | <i>P</i> $\bar{1}$                | 9    |
| 10  | Pb <sub>2</sub> V <sub>3</sub> Se <sub>5</sub> O <sub>18</sub>   | 0D        | [VO <sub>6</sub> ]                    | Pnma                              | 9    |
| 11  | ScVSe <sub>2</sub> O <sub>8</sub>  | 0D        | [V <sub>2</sub> O <sub>10</sub> ]     | <i>P2</i> <sub>1</sub> / <i>c</i> | 10   |
| 12  | ScVSe <sub>2</sub> O <sub>8</sub>  | 0D        | [V <sub>2</sub> O <sub>7</sub> ]      | <i>P2</i> <sub>1</sub> / <i>c</i> | 10   |
| 13  | Sr <sub>2</sub> (VO) <sub>3</sub> (SeO <sub>3</sub> ) <sub>5</sub>   | 0D        | [VO <sub>6</sub> ]                    | Pnma                              | 11   |
| 14  | Ba <sub>3</sub> (VO <sub>2</sub> ) <sub>2</sub> (SeO <sub>3</sub> ) <sub>4</sub>                                   | 0D        | [VO <sub>5</sub> ]                    | <i>P2</i> <sub>1</sub> / <i>c</i> | 11   |
| 15  | Sr <sub>2</sub> (VO <sub>2</sub> ) <sub>2</sub> (SeO <sub>3</sub> ) <sub>3</sub>                                   | 0D        | [VO <sub>5</sub> ]+[VO <sub>6</sub> ] | <i>P2</i> <sub>1</sub> / <i>c</i> | 12   |
| 16  | Sr <sub>4</sub> (VO <sub>2</sub> ) <sub>2</sub> (SeO <sub>3</sub> ) <sub>4</sub> (Se <sub>2</sub> O <sub>5</sub> ) | 0D        | [VO <sub>5</sub> ]                    | <i>Fdd2</i>                       | 12   |
| 17  | Pb <sub>4</sub> (VO <sub>2</sub> ) <sub>2</sub> (SeO <sub>3</sub> ) <sub>4</sub> (Se <sub>2</sub> O <sub>5</sub> ) | 0D        | [VO <sub>5</sub> ]                    | <i>Fdd2</i>                       | 12   |
| 18  | (V <sub>2</sub> O <sub>3</sub> )(SeO <sub>3</sub> ) <sub>2</sub>   | 0D        | [V <sub>4</sub> O <sub>18</sub> ]     | <i>P2</i> <sub>1</sub> / <i>c</i> | 13   |
| 19  | Pb <sub>2</sub> (VO)(SeO <sub>3</sub> ) <sub>3</sub>   | 0D        | [VO <sub>6</sub> ]                    | <i>P2</i> <sub>1</sub> / <i>c</i> | 13   |
| 20  | VOSe <sub>2</sub> O <sub>5</sub>   | 1D        | [VO <sub>6</sub> ]                    | <i>P4cc</i>                       | 14   |
| 21  | VO(SeO <sub>3</sub> )  | 1D        | [VO <sub>6</sub> ]                    | <i>P2</i> <sub>1</sub> / <i>c</i> | 15   |
| 22  | K(V <sub>2</sub> SeO <sub>7</sub> )  | 1D        | [VO <sub>4</sub> ]+[VO <sub>6</sub> ] | Pnma                              | 16   |
| 23  | Rb(V <sub>2</sub> SeO <sub>7</sub> )   | 1D        | [VO <sub>4</sub> ]+[VO <sub>6</sub> ] | Pnma                              | 17   |
| 24  | TlSeVO <sub>5</sub>  | 1D        | [VO <sub>6</sub> ]                    | <i>Pna2</i> <sub>1</sub>          | 18   |

|    |  |    |   |                         |    |
|----|--|----|---|-------------------------|----|
| 25 | Th(VO <sub>3</sub> ) <sub>2</sub> (SeO <sub>3</sub> )                              | 1D | [VO <sub>5</sub> ]  | <i>Pbcm</i>             | 19 |
| 26 | La <sub>5</sub> V <sub>3</sub> Se <sub>6</sub> O <sub>7</sub>                      | 1D | [VSe <sub>4</sub> O <sub>2</sub> ]                        | <i>Pmmn</i>             | 20 |
| 27 | La <sub>7</sub> VSe <sub>5</sub> O <sub>7</sub>                                    | 1D | [VSe <sub>4</sub> O <sub>2</sub> ]                        | <i>Cmcm</i>             | 20 |
| 28 | La <sub>13</sub> V <sub>7</sub> Se <sub>16</sub> O <sub>15</sub>                   | 1D | [VSe <sub>4</sub> O <sub>2</sub> ] + [VSe <sub>5</sub> O] | <i>Cmc2<sub>1</sub></i> | 20 |
| 29 | Bi <sub>2</sub> V <sub>2</sub> Se <sub>4</sub> O <sub>16</sub>                     | 1D | [VO <sub>6</sub> ]  | <i>P2<sub>1</sub>/c</i> | 9  |
| 30 | ZnV(Se <sub>2</sub> O <sub>7</sub> )   | 1D | [VO <sub>5</sub> ] + [VO <sub>6</sub> ]                   | <i>P2<sub>1</sub>/c</i> | 21 |
| 31 | Cd <sub>6</sub> V <sub>2</sub> Se <sub>5</sub> O <sub>21</sub>                     | 1D | [VO <sub>4</sub> ]  | <i>P2<sub>1</sub>/c</i> | 21 |
| 32 | InVSe <sub>2</sub> O <sub>8</sub>  | 1D | [VO <sub>5</sub> ]  | <i>Pm</i>               | 22 |
| 33 | Co <sub>2</sub> V <sub>2</sub> Se <sub>2</sub> O <sub>11</sub>                     | 1D | [VO <sub>5</sub> ] + [VO <sub>6</sub> ]                   | <i>P2<sub>1</sub>/m</i> | 23 |
| 34 | Eu(VSe <sub>2</sub> O <sub>8</sub> )   | 1D | [VO <sub>5</sub> ]  | <i>P2<sub>1</sub>/m</i> | 24 |
| 35 | Gd(VSe <sub>2</sub> O <sub>8</sub> )   | 1D | [VO <sub>6</sub> ]  | <i>P2<sub>1</sub>/m</i> | 24 |
| 36 | Tb(VSe <sub>2</sub> O <sub>8</sub> )   | 1D | [VO <sub>6</sub> ]  | <i>P2<sub>1</sub>/m</i> | 24 |
| 37 | V <sub>2</sub> Se <sub>2</sub> O <sub>9</sub>                                      | 2D | [VO <sub>6</sub> ]  | <i>P2<sub>1</sub>/c</i> | 25 |
| 38 | (NH <sub>4</sub> )(VO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> | 2D | [VO <sub>6</sub> ]  | <i>P6<sub>3</sub></i>   | 26 |
| 39 | K(VO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub>                  | 2D | [VO <sub>6</sub> ]  | <i>P6<sub>3</sub></i>   | 27 |
| 40 | Rb(Se <sub>2</sub> V <sub>3</sub> O <sub>12</sub> )                                | 2D | [VO <sub>6</sub> ]  | <i>P6<sub>3</sub></i>   | 28 |
| 41 | Tl(Se <sub>2</sub> V <sub>3</sub> O <sub>12</sub> )                                | 2D | [VO <sub>6</sub> ]  | <i>P6<sub>3</sub></i>   | 28 |
| 42 | Cs(VO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub>                 | 2D | [VO <sub>6</sub> ]  | <i>P6<sub>3</sub></i>   | 29 |
| 43 | YVSe <sub>2</sub> O <sub>8</sub>   | 2D | [VO <sub>6</sub> ]  | <i>Abm2</i>             | 30 |
| 44 | LaVSe <sub>2</sub> O   | 2D | [VSe <sub>4</sub> O <sub>2</sub> ] + [VSe <sub>6</sub> ]  | <i>C2/m</i>             | 20 |
| 45 | La <sub>5</sub> V <sub>3</sub> Se <sub>7</sub> O <sub>5</sub>                      | 2D | [VSe <sub>4</sub> O <sub>2</sub> ] + [VSe <sub>6</sub> ]  | <i>Pnma</i>             | 20 |
| 46 | Ba(V <sub>2</sub> O <sub>5</sub> )(SeO <sub>3</sub> )                              | 2D | [VO <sub>5</sub> ] + [VO <sub>6</sub> ]                   | <i>Pnma</i>             | 12 |
| 47 | AgV(SeO <sub>5</sub> )   | 2D | [VO <sub>4</sub> ]  | <i>Pbcm</i>             | 31 |



**Figure S1.** (a) Energy dispersive X-ray spectroscopy (EDS) analysis for  $K_2Zn_3Se_4O_{12}$ .

(b) Energy dispersive X-ray spectroscopy (EDS) analysis for  $K_4Zn_3V_4Se_2O_{18}$ .

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