Electronic Supporting Information

Antimony-dependent Expansion for the Keggin Heteropolyniobate Family

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Section 1

Experimental Section

Materials and methods

All chemicals were obtained from commercial sources and were used without further purification. $K_7HNb_6O_{19}\cdot 13H_2O$ was prepared according to the literature[1] and its identity was confirmed by its IR spectrum. Elemental analysis for C, H and N was performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Elemental analyses for As, Cu, Ge, Nb, P, Sb, Si and V were performed with a Leaman inductively coupled plasma (ICP) spectrometer. Fourier transform infrared (FTIR) spectra were recorded in the range 4000-400 cm^{-1} on an Alpha Centauri FTIR spectrophotometer from samples in KBr pellets. UV/Vis diffuse reflection spectra were recorded on a Cary 500 UV/Vis spectrophotometer from samples in $BaSO_4$ pellets. Energy-dispersive X-ray spectroscopy (EDX) was acquired with an XL30 Field-Emission Environmental Scanning Electron Microscope. X-ray powder diffraction (XRPD) data were recorded over the 2θ range from 5 to 50° at room temperature on a Siemens D5005 diffract meter with Cu-$K\alpha$ radiation (λ = 1.5418Å). Thermo gravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer by heating from room temperature to 800 °C at a rate of 5 °C·min^{-1} under nitrogen.

Synthesis of $[Cu(en)_2(H_2O)]_4[H_2SiNb_{12}O_{40}Sb_2]\cdot 18H_2O$ (1-Si) In 8mL distilled water, 0.0520 g $Cu(CH_3COO)_2\cdot 2H_2O$ (0.25 mmol), 0.1256g ethanediamine (en) (1.6 mmol), 0.0288g $Na_2SiO_3\cdot 9H_2O$ (0.1mmol), 0.1169g Sb_2O_3 (0.4 mmol) and 0.0695g $K_7HNb_6O_{19}\cdot 13H_2O$ (0.05mmol) were dissolved with sufficient stirring. The resulting blue solution was adjusted to pH 11.50 with a 3M KOH solution, and it was then transferred to a Teflon-lined stainless steel autoclave (23 mL). The autoclave was heated at 120 °C for 72 h, and then cooled to room temperature at a rate of 10 °C h^{-1}, and filtered. The filtrate was kept undisturbed in a 25mL beaker for 3 h at room temperature. Blue sheet crystals of **1-Si** were obtained. (Yield, 11.7% based on Nb). Elemental analysis calcd (%) for **1-Si**: C 6.08, H 3.51, N 7.09; Cu 8.04, Si 0.89, Sb 7.71, Nb 35.28; found: C 6.20, H 3.38, N 7.20; Cu 7.95, Si 0.81, Sb 7.59, Nb 35.15. IR (cm^{-1}): 3302 (s), 3219 (s), 3136 (s), 2965 (m), 2361 (m), 1639 (m), 1584 (m), 1460 (w), 1279 (w), 1105 (w), 1045 (s), 939 (m), 864 (s), 812 (s), 679 (s), 523 (m), 482 (m).

Synthesis of $[Cu(en)_2(H_2O)]_4[H_2GeNb_{12}O_{40}Sb_2]\cdot 18H_2O$ (1-Ge). The synthesis method for **1-Ge** was the same as that described above for **1-Si**, but GeO_2 (0.01g, 0.1mmol) was used instead of $Na_2SiO_3\cdot 9H_2O$. Blue sheet crystals of **1-Ge** were obtained. (Yield, 12.5% based on Nb). Elemental analysis calcd (%) for **1-Ge**: C 6.00, H 3.46, N 6.99; Cu 7.93, Ge 2.27, Sb 7.60, Nb 34.79; found: C 5.87, H 3.34, N 6.89; Cu 7.82, Ge 2.17, Sb 7.71, Nb 34.66. IR (cm^{-1}): 3422 (s), 3246 (m), 3136 (m), 2924 (m), 1632 (m), 1587 (m), 1460 (w), 1396 (w), 1325 (w), 1279 (w), 1178 (w), 1109 (w), 1045 (m), 1015 (m), 874 (m), 812 (m), 764 (s), 683(s), 478 (m).

Synthesis of $[Cu(en)_2(H_2O)]_4[HPNb_{12}O_{40}Sb_2]\cdot 18H_2O$ (1-P). The synthesis method for **1-P** was the same as that described for **1-Si**, but $NaH_2PO_4\cdot 2H_2O$ (0.0162g, 0.1mmol) was used instead of $Na_2SiO_3\cdot 9H_2O$. Blue sheet crystals of **1-P** were obtained. (Yield, 10.5% based on Nb). Elemental analysis calcd (%) for **1-P**: C 6.08, H 3.47, N 7.09; Cu 8.04, P 0.98, Sb 7.70, Nb 35.26; found: C 6.00, H 3.39, N 7.00; Cu 7.94, P 0.91, Sb 7.95, Nb 35.12. IR (cm^{-1}): 3385 (s), 3300 (s), 3223 (s), 3138 (s), 2951 (m), 2361 (m), 2342 (m), 1632 (m), 1585 (m), 1460 (w), 1385 (w), 1279 (w), 1178 (w), 1107 (w), 1045 (s), 1015 (s), 876 (s), 756 (s), 684 (s), 478 (m).

Synthesis of $[Cu(en)_2(H_2O)]_4[HAsNb_{12}O_{40}Sb_2]\cdot 18H_2O$ (1-As). The synthesis method for **1-As** was the same as that described for **1-Si**, but $Na_2HAsO_4\cdot 7H_2O$ (0.0323g, 0.1mmol) was used instead of $Na_2SiO_3\cdot 9H_2O$. Blue sheet crystals of **1-As** were obtained. (Yield, 9.3% based on Nb). Elemental analysis calcd (%) for **1-As**: C 5.99, H 3.43, N 6.99; Cu 7.93, As 2.34, Sb 7.60, Nb 34.78; found: C 6.10, H 3.35, N 7.10; Cu 7.81, As 2.27, Sb 7.53, Nb 34.68. IR (cm^{-1}): 3406 (s), 3238 (s), 3138 (s), 2951 (m), 2342 (m), 1630 (m), 1591 (m), 1460 (w), 1279 (w), 1180 (w), 1105 (w), 1045 (m), 986 (w), 933 (m), 877 (m), 815 (s), 746 (m), 669 (s), 511 (w), 476 (m), 445 (m).

Synthesis of $[Cu(en)_2(H_2O)]_4[HVNb_{12}O_{40}Sb_2]\cdot 18H_2O$ (1-V). The synthesis method for **1-V** was the same as that described for **1-Si**, but V_2O_5 (0.0101g, 0.05mmol) was used instead of $Na_2SiO_3\cdot 9H_2O$. Blue sheet crystals of **1-V** were obtained. (Yield, 9.1% based on Nb). Elemental analysis calcd (%) for **1-V**: C 6.04, H 3.45, N 7.04; Cu 7.99, V 1.60, Sb 7.65, Nb 35.04; found: C 5.94, H 3.31, N 6.93; Cu 7.88, V 1.51, Sb 7.54, Nb 34.95 IR (cm^{-1}): 3419.70 (s), 3240.32 (s), 3134.24 (s), 2939.44 (m), 2362.73

(m), 1635.59 (m), 1587.37 (m), 1458.14 (m), 1398.35 (w), 1276.84 (w), 1182.33 (w), 1105.18 (w), 1045.39 (m), 935.45 (m), 877.59 (m), 790.79 (s), 667.35 (s), 538.13 (w), 472.55 (w).

Synthesis of $[Cu(en)_2]_3[Cu(en)_2(H_2O)]_4\{[Cu(en)_2]_2[HSiNb_{12}O_{40}Sb_2]_2\}\cdot 18H_2O$ (2-Si). The synthesis method for **2-Si** was the same as that described for **1-Si**, but the amount of $Cu(CH_3COO)_2\cdot 2H_2O$ and en was doubled. Purple needle-shape crystals of **2-Si** were obtained. (Yield, 15.8% based on Nb). Elemental analysis calcd (%) for **2-Si**: C 7.08, H 3.14, N 8.26; Cu 9.37, Si 0.92, Sb 7.98, Nb 36.52; found: C 7.01, H 3.03, N 8.19; Cu 9.47, Si 0.83, Sb 8.06, Nb 36.64. IR (cm^{-1}): 3373.41(s), 3300.12 (s), 3219.11 (s), 3132.32 (s), 2360.81 (m), 1633.67 (m), 1583.52 (m), 1456.22 (w), 1278.77 (w), 1166.90 (w), 1105.18 (w), 1045.39 (m), 975.96 (w), 937.38 (m), 856.37(m), 810.08 (s), 669.28 (s), 522.70 (m), 482.19 (m).

Synthesis of $[Cu(en)_2]_3[Cu(en)_2(H_2O)]_4\{[Cu(en)_2]_2[HGeNb_{12}O_{40}Sb_2]_2\}\cdot 18H_2O$ (2-Ge). The synthesis method for **2-Ge** was the same as that described for **1-Ge**, but the amount of $Cu(CH_3COO)_2\cdot 2H_2O$ and en was doubled. Purple needle-shape crystals of **2-Ge** were obtained. (Yield, 13.4% based on Nb). Elemental analysis calcd (%) for **2-Ge**: C 6.98, H 3.09, N 8.14; Cu 9.23, Ge 2.35, Sb 7.86, Nb 36.00; found: C 6.87, H 3.00, N 8.11; Cu 9.32, Ge 2.42, Sb 7.94, Nb 36.13. IR (cm^{-1}): 3410.06 (s), 3307.84 (s), 3221.04 (s), 3134.25 (m), 2360.81 (m), 1631.74 (m), 1583.52 (m), 1456.22 (w), 1278.77 (w), 1170.76 (w), 1107.11 (w), 1045.39 (m), 985.60 (w), 920.02 (w), 856.37 (m), 731.00 (m), 669.28 (s), 524.62 (w), 474.48 (w), 433.97 (w).

Synthesis of $[Cu(en)_2]\{[Cu(en)_2]_3[SiNb_{12}O_{39}Sb_2]\}\cdot 11H_2O$ (3-Si). The synthesis method for **3-Si** was the same as that described for **1-Si**, but the temperature of autoclave was changed from 120 °C to 165 °C. Blue block crystals of **3-Si** were directly obtained. (Yield, 16.8% based on Nb). Elemental analysis calcd (%) for **3-Si**: C 6.53, H 2.94, N 7.61; Cu 8.64, Si 0.95, Sb 8.27, Nb 37.87; found: C 6.45, H 2.81, N 7.51; Cu 8.85, Si 0.86, Sb 8.16, Nb 37.74. IR (cm^{-1}): 3406.2 (s), 3238.39 (s), 3132.31 (s), 2949.08 (s), 2360.81 (w), 1635.59 (m), 1589.30 (m), 1458.14 (w), 1278.77 (w), 1178.47 (w), 1103.25 (w), 1045.39 (m), 941.24 (m), 866.02 (m), 840.94 (m), 810.08 (m), 686.64 (s), 522.70 (m), 482.19 (m).

Synthesis of $[Cu(en)_2]\{[Cu(en)_2]_3[GeNb_{12}O_{39}Sb_2]\}\cdot 11H_2O$ (3-Ge). The synthesis method for **3-Ge** was the same as that described for **1-Ge**, but the temperature of autoclave was changed from 120 °C to 165 °C. Blue block crystals of **3-Ge** were directly obtained. (Yield, 17.7% based on Nb). Elemental analysis calcd (%) for **3-Ge**: C 6.43, H 2.90, N 7.50; Cu 8.51, Ge 2.43, Sb 8.15, Nb 37.31; found: C 6.36, H 2.81, N 7.42; Cu 8.62, Si 2.50, Sb 8.08, Nb 37.19. IR (cm^{-1}): 3404.27 (s), 3236.47 (s), 3134.25 (s), 2949.08 (m), 2356.95 (m), 1633.67 (m), 1589.30 (m), 1456.22 (w), 1278.77 (w), 1176.55 (w), 1103.25 (w), 1045.39 (m), 921.95 (w), 866.02 (m), 798.51 (m), 748.36 (s), 678.93 (s), 526.55 (w), 480.26 (m).

X-ray Crystallographic Study. The crystal data for all the compounds were collected on a Bruker SMART-CCD diffractometer with graphite-monochromated Mo-*Kα* radiation (λ = 0.71069 Å) at 293 K. All structures were solved by direct methods and refined by full matrix least squares on F^2 using the *SHELXTL-97* crystallographic software package.[2] The positions of hydrogen atoms on carbon atoms and nitrogen atoms were calculated theoretically. The numbers of lattice water molecules for all compounds were estimated by the results of elemental analyses and TG curves. H atoms have been added to the molecular formula to balance the charges. The crystal data and structure refinements of all the compounds are summarized in Table S1 and Table S2. Crystallographic data has been deposited with the Cambridge Crystallography Data Centre (CCDC) as deposition numbers CCDC 971581, 1020912, 1020913, 1020914, 1034783, 1034782, 1025243, 1034781 and 1034780 for compounds all the compounds, respectively. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. *via* fax (+44 1223 336033) or e-mail (deposit@ccdc.cam.ac.uk).

1. C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 332-334.
2. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure*; University of Gottingen: Göttingen, Germany, **1993**.

Table S1. Crystal data for **1**.

Compound	**1-Si**	**1-Ge**	**1-P**	**1-As**	**1-V**
Formula	$C_{16}H_{110}N_{16}O_{62}Cu_4Nb_{12}Sb_2Si$	$C_{16}H_{110}N_{16}O_{62}Cu_4GeNb_{12}Sb_2$	$C_{16}H_{109}N_{16}O_{62}Cu_4Nb_{12}PSb_2$	$C_{16}H_{109}N_{16}O_{62}AsCu_4Nb_{12}Sb_2$	$C_{16}H_{109}N_{16}O_{62}Cu_4Nb_{12}Sb_2V$
M_r	3159.87	3204.37	3161.74	3205.69	3181.71
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$
a/Å	25.6450(5)	25.5410(4)	25.6100(5)	25.6050(5)	25.7020(5)
b/Å	25.6450(5)	25.5410(4)	25.6100(5)	25.6050(5)	25.7020(5)
c/Å	16.2100(5)	16.1450(4)	16.1860(6)	16.1890(5)	16.2360(6)
α/deg.	90	90	90	90	90
β/deg.	90	90	90	90	90
γ/deg.	90	90	90	90	90
V, Å^3	10660.8(4)	10532.1(4)	10615.9(5)	10613.8(4)	10725.4(5)
Z	4	4	4	4	4
D_c/Mg·m^{-3}	1.969	2.021	1.978	2.006	1.970
μ/mm^{-1}	2.612	2.912	2.627	2.922	2.667
F(000)	6152	6224	6152	6224	6184
θ range/deg	2.18-28.37	3.14-25.00	3.13-25.00	3.18-24.99	3.36-24.99
Reflections collected	35081	19047	19856	18769	18533
Reflections unique [R_{int}]	6678 [0.1125]	4616 [0.0290]	4655 [0.0540]	4641 [0.0343]	4724 [0.0389]
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0581, 0.1624	0.0376, 0.1174	0.0477, 0.1325	0.0402, 0.1220	0.0418, 0.1278
R_1[a], wR_2[b] (all data)	0.1175, 0.1924	0.0477, 0.1245	0.0737, 0.1458	0.0514, 0.1313	0.0550, 0.1351
Goodness-of-fit[c]	1.037	1.088	1.073	1.040	1.091

Table S2. Crystal data for **2** and **3**.

Compound	**2-Si**[d]	**2-Ge**[d]	**3-Si**	**3-Ge**
Formula	$C_{36}H_{190}N_{36}O_{102}Cu_9Nb_{24}Sb_4Si_2$	$C_{36}H_{190}N_{36}O_{102}Cu_9Ge_2Nb_{24}Sb_4$	$C_{16}H_{86}N_{16}O_{50}Cu_4Nb_{12}Sb_2Si$	$C_{16}H_{86}N_{16}O_{50}Cu_4GeNb_{12}Sb_2$
M_r	6105.12	6194.12	2943.68	2988.18
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	14.7450(5)	14.8930(8)	13.9137(7)	13.8690(6)
b/Å	40.0530(14)	39.874(2)	14.4730(7)	14.6210(6)
c/Å	19.1580(7)	19.3320(11)	21.9355(10)	22.1360(9)
α/deg.	90	90	84.8190(10)	84.6380(10)
β/deg.	94.8120(10)	95.0520(10)	79.8390(10)	80.6320(10)
γ/deg.	90	90	61.3420(10)	62.3180(10)
V, Å^3	11274.5(7)	11435.6(11)	3815.2(3)	3921.1(3)
Z	2	2	2	2
D_c/g cm^{-3}	1.798	1.799	2.562	2.531
μ/mm^{-1}	2.551	2.762	3.628	3.891
F(000)	5902	5974	2836	2872
θ range/deg	1.47- 23.28	1.47-27.24	1.60-28.31	1.67-28.31
Reflections collected	48284	78111	28356	29267
Reflections unique [R_{int}]	16230 [0.0491[d]]	25520 [0.0574[d]]	18856 [0.0285]	19381 [0.0219]
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0493, 0.1337	0.0634, 0.1960	0.0528, 0.1339	0.0425, 0.1254
R_1[a], wR_2[b] (all data)	0.0665, 0.1413	0.0909, 0.2111	0.0838, 0.1581	0.0576, 0.1383
Goodness-of-fit[c]	1.015	1.053	1.038	1.047

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$. [c] Goodness-of-fit = $\{\sum[w(F_o^2 - F_c^2)^2] / [n_{obs} - n_{param}]\}^{1/2}$. [d] R indices of compound **2-Si** and **2-Ge** are computed after SQUEEZE.

Section 2

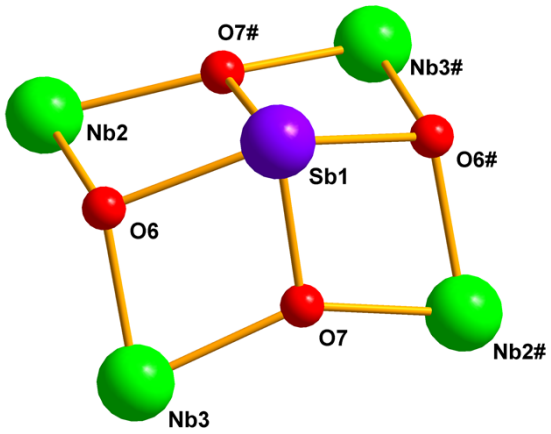

Fig. S1 Coordination mode of Sb^{3+} in **1**. (Color code: green, Nb; purple, Sb; red, O)

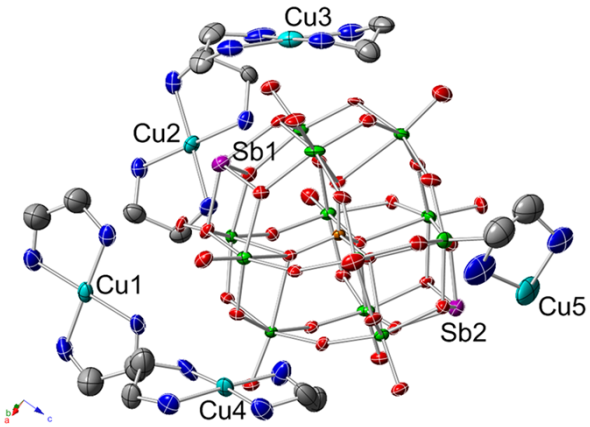

Fig. S2 Thermal ellipsoid representation of $[\alpha\text{-HTNb}_{12}O_{38}Sb_2]^{9-}$ (T = Si or Ge) polyanion in **2** (occupancy 0.5 of Cu5). (Color code: orange, T; green, Nb; purple, Sb; red, O; light blue, Cu; blue, N; gray, C) (50% probability for the ellipsoids)

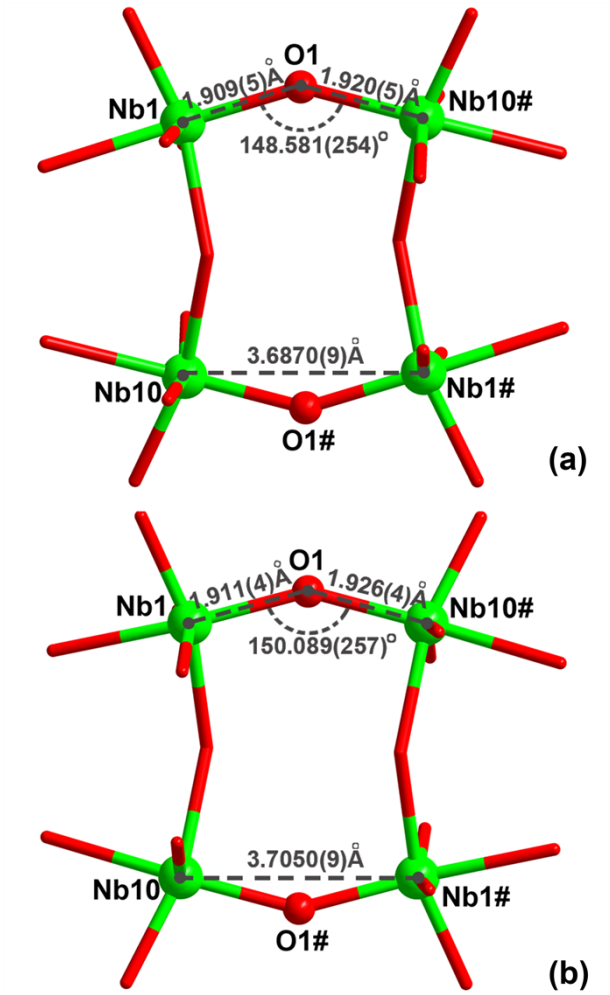

Fig. S3 Bond lengths of Nb-μ_2-O and bond angles of Nb-μ_2-O-Nb: (a) **3-Si**; (b) **3-Ge**. (color code: green, NbO_6; red, O)

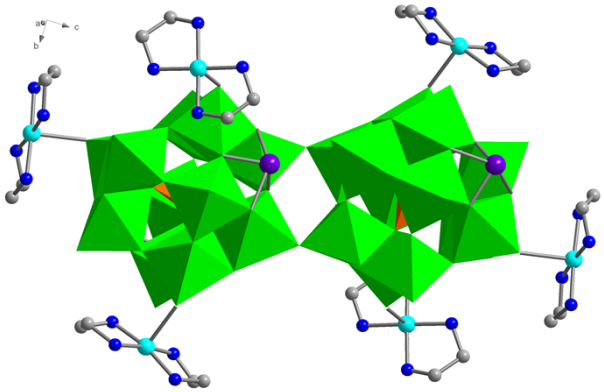

Fig. S4 $[Cu(en)_2]^{2+}$ decorate $\{TNb_{12}O_{39}Sb_2\}$ (T = Si or Ge) cluster *via* weak Cu-O_t coordination interactions in **3**. (color code: orange, TO_4; green, NbO_6; purple, Sb; red, O; light blue, Cu; blue, N; gray, C)

Section 3

Table S3. Selected bond lengths [Å] for **1-Si** and **1-Ge**.

	1-Si		**1-Ge**	
$Nb\text{-}O_t$	Nb(1)-O(1)	1.770(6)	Nb(1)-O(1)#2	1.754(5)
	Nb(2)-O(2)	1.776(6)	Nb(2)-O(2)	1.754(5)
	Nb(3)-O(3)	1.768(6)	Nb(3)-O(3)	1.757(5)
$Nb\text{-}O_b$	Nb(1)-O(4)	2.011(6)	Nb(1)-O(4)	1.993(4)
	Nb(1)-O(5)	2.000(6)	Nb(1)-O(5)	2.010(4)
	Nb(2)-O(5)	1.919(6)	Nb(2)-O(5)	1.902(4)
	Nb(2)-O(6)	2.105(6)	Nb(2)-O(6)	2.088(4)
	Nb(3)-O(4)	1.904(6)	Nb(3)-O(4)	1.904(4)
	Nb(3)-O(6)	2.080(6)	Nb(3)-O(6)	2.097(4)
	Nb(1)-O(8)	1.943(6)	Nb(1)-O(8)#1	1.961(4)
	Nb(1)-O(9)	1.953(6)	Nb(1)-O(9)#2	1.939(4)
	Nb(2)-O(7)	2.112(6)	Nb(2)-O(7)#3	2.114(4)
	Nb(2)-O(9)#3	1.898(6)	Nb(2)-O(9)	1.890(4)
	Nb(3)-O(7)#1	2.112(6)	Nb(3)-O(7)	2.109(4)
	Nb(3)-O(8)#2	1.894(6)	Nb(3)-O(8)	1.886(4)
$Nb\text{-}O_c$	Nb(1)-O(10)	2.465(6)	Nb(1)-O(10)	2.443(4)
	Nb(2)-O(10)	2.425(6)	Nb(2)-O(10)	2.414(4)
	Nb(3)-O(10)	2.427(6)	Nb(3)-O(10)	2.408(4)
$T\text{-}O_c$	Si(1)-O(10)	1.631(6)	Ge(1)-O(10)	1.704(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1/2,z #2 -y+1/4,x+1/4,-z+1/4 #3 y-1/4,-x+1/4,-z+1/4

O_t: terminal oxygen; O_b: bridging oxygen; O_c: central oxygen.

Table S4. Selected bond lengths [Å] for **1-P**, **1-As** and **1-V**.

	1-P		**1-As**		**1-V**	
Nb-O_t	Nb(1)-O(1)#1	1.760(6)	Nb(1)-O(1)	1.756(5)	Nb(1)-O(1)	1.764(5)
	Nb(2)-O(2)	1.749(6)	Nb(2)-O(2)	1.759(5)	Nb(2)-O(2)	1.758(5)
	Nb(3)-O(3)	1.769(6)	Nb(3)-O(3)	1.760(5)	Nb(3)-O(3)	1.764(5)
Nb-O_b	Nb(1)-O(4)	1.999(6)	Nb(1)-O(4)	1.995(5)	Nb(1)-O(4)#1	1.998(5)
	Nb(1)-O(5)	2.006(6)	Nb(1)-O(5)	2.017(5)	Nb(1)-O(5)	2.021(5)
	Nb(2)-O(5)	1.906(5)	Nb(2)-O(5)	1.907(5)	Nb(2)-O(5)#1	1.913(5)
	Nb(2)-O(6)	2.082(6)	Nb(2)-O(6)	2.097(5)	Nb(2)-O(6)	2.099(5)
	Nb(3)-O(4)	1.909(6)	Nb(3)-O(4)	1.912(5)	Nb(3)-O(4)	1.920(5)
	Nb(3)-O(6)	2.106(6)	Nb(3)-O(6)	2.104(5)	Nb(3)-O(6)#2	2.107(5)
	Nb(1)-O(8)#2	1.940(6)	Nb(1)-O(8)	1.967(5)	Nb(1)-O(8)	1.978(5)
	Nb(1)-O(9)#1	1.963(6)	Nb(1)-O(9)	1.946(5)	Nb(1)-O(9)	1.942(5)
	Nb(2)-O(7)	2.116(5)	Nb(2)-O(7)#1	2.115(5)	Nb(2)-O(7)	2.127(4)
	Nb(2)-O(8)	1.890(6)	Nb(2)-O(9)#2	1.892(5)	Nb(2)-O(9)	1.904(5)
	Nb(3)-O(7)#3	2.105(5)	Nb(3)-O(7)	2.111(5)	2.113(4)	2.113(4)
	Nb(3)-O(9)	1.884(6)	Nb(3)-O(8)#3	1.890(5)	1.886(5)	1.886(5)
Nb-O_c	Nb(1)-O(10)	2.530(5)	Nb(1)-O(10)	2.463(4)	2.448(4)	2.448(4)
	Nb(2)-O(10)	2.489(6)	Nb(2)-O(10)	2.439(4)	2.425(4)	2.425(4)
	Nb(3)-O(10)	2.471(5)	Nb(3)-O(10)	2.427(4)	2.406(4)	2.406(4)
T-O_c	P(1)-O(10)	1.590(6)	As(1)-O(10)	1.688(4)	V(1)-O(10)	1.724(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1/2,z #2 -y+1/4,x+1/4,-z+1/4 #3 y-1/4,-x+1/4,-z+1/4

O_t: terminal oxygen; O_b: bridging oxygen; O_c: central oxygen.

Table S5. Selected bond lengths [Å] for **2**.

	2-Si		**2-Ge**	
Nb-O_t	Nb(1)-O(1)	1.769(8)	Nb(1)-O(1)	1.778(7)
	Nb(2)-O(2)	1.763(9)	Nb(2)-O(2)	1.787(7)
	Nb(3)-O(3)	1.771(9)	Nb(3)-O(3)	1.766(6)
	Nb(4)-O(4)	1.782(9)	Nb(4)-O(4)	1.778(7)
	Nb(5)-O(5)	1.766(9)	Nb(5)-O(5)	1.779(7)
	Nb(6)-O(6)	1.777(8)	Nb(6)-O(6)	1.773(7)
	Nb(7)-O(7)	1.782(8)	Nb(7)-O(7)	1.772(7)
	Nb(8)-O(8)	1.746(8)	Nb(8)-O(8)	1.751(7)

	Nb(9)-O(9)	1.787(8)	Nb(9)-O(9)	1.783(6)
	Nb(10)-O(10)	1.793(8)	Nb(10)-O(10)	1.797(6)
	Nb(11)-O(11)	1.775(8)	Nb(11)-O(11)	1.761(7)
	Nb(12)-O(12)	1.763(8)	Nb(12)-O(12)	1.759(6)
	Nb(1)-O(13)	1.926(9)	Nb(1)-O(13)	1.906(7)
	Nb(1)-O(15)	2.070(8)	Nb(1)-O(15)	2.093(6)
	Nb(1)-O(25)	2.116(8)	Nb(1)-O(25)	2.129(6)
	Nb(1)-O(26)	1.907(8)	Nb(1)-O(26)	1.898(6)
	Nb(2)-O(13)	2.023(9)	Nb(2)-O(13)	2.037(7)
	Nb(2)-O(14)	2.000(8)	Nb(2)-O(14)	2.011(6)
	Nb(2)-O(27)	1.972(9)	Nb(2)-O(27)	1.973(6)
	Nb(2)-O(28)	1.949(8)	Nb(2)-O(28)	1.952(7)
	Nb(3)-O(14)	1.921(8)	Nb(3)-O(14)	1.917(6)
	Nb(3)-O(15)	2.068(8)	Nb(3)-O(15)	2.092(6)
	Nb(3)-O(29)	1.902(8)	Nb(3)-O(29)	1.896(6)
	Nb(3)-O(30)	2.108(8)	Nb(3)-O(30)	2.113(6)
	Nb(4)-O(16)	1.930(8)	Nb(4)-O(16)	1.918(7)
	Nb(4)-O(18)	2.070(8)	Nb(4)-O(18)	2.107(6)
	Nb(4)-O(27)	1.925(9)	Nb(4)-O(27)	1.898(6)
	Nb(4)-O(32)	2.081(8)	Nb(4)-O(32)	2.125(7)
$Nb\text{-}O_b$	Nb(5)-O(16)	2.009(9)	Nb(5)-O(16)	2.011(7)
	Nb(5)-O(17)	1.987(8)	Nb(5)-O(17)	1.988(6)
	Nb(5)-O(26)	1.978(8)	Nb(5)-O(26)	1.965(6)
	Nb(5)-O(31)	1.940(8)	Nb(5)-O(31)	1.968(7)
	Nb(6)-O(17)	1.912(8)	Nb(6)-O(17)	1.914(6)
	Nb(6)-O(18)	2.078(8)	Nb(6)-O(18)	2.096(6)
	Nb(6)-O(34)	2.087(8)	Nb(6)-O(34)	2.117(6)
	Nb(6)-O(35)	1.892(8)	Nb(6)-O(35)	1.891(6)
	Nb(7)-O(19)	1.928(8)	Nb(7)-O(19)	1.928(6)
	Nb(7)-O(20)	2.079(8)	Nb(7)-O(20)	2.092(6)
	Nb(7)-O(28)	1.902(8)	Nb(7)-O(28)	1.900(6)
	Nb(7)-O(32)	2.092(8)	Nb(7)-O(32)	2.093(6)
	Nb(8)-O(19)	1.991(8)	Nb(8)-O(19)	2.000(6)
	Nb(8)-O(21)	2.007(8)	Nb(8)-O(21)	2.014(6)
	Nb(8)-O(29)	1.945(8)	Nb(8)-O(29)	1.954(6)
	Nb(8)-O(33)	1.991(8)	Nb(8)-O(33)	1.982(6)
	Nb(9)-O(20)	2.079(8)	Nb(9)-O(20)	2.103(6)

	Nb(9)-O(21)	1.914(8)	Nb(9)-O(21)	1.910(6)
	Nb(9)-O(34)	2.097(8)	Nb(9)-O(34)	2.105(6)
	Nb(9)-O(36)	1.901(8)	Nb(9)-O(36)	1.892(6)
	Nb(10)-O(22)	2.083(8)	Nb(10)-O(22)	2.103(6)
	Nb(10)-O(23)	1.912(8)	Nb(10)-O(23)	1.906(6)
	Nb(10)-O(30)	2.077(8)	Nb(10)-O(30)	2.113(6)
	Nb(10)-O(33)	1.898(8)	Nb(10)-O(33)	1.882(6)
	Nb(11)-O(22)	2.082(8)	Nb(11)-O(22)	2.100(6)
	Nb(11)-O(24)	1.920(8)	Nb(11)-O(24)	1.907(6)
	Nb(11)-O(25)	2.083(8)	Nb(11)-O(25)	2.110(6)
	Nb(11)-O(31)	1.911(8)	Nb(11)-O(31)	1.891(6)
	Nb(12)-O(23)	2.015(8)	Nb(12)-O(23)	2.018(6)
	Nb(12)-O(24)	1.979(8)	Nb(12)-O(24)	2.010(6)
	Nb(12)-O(35)	1.954(8)	Nb(12)-O(35)	1.964(6)
	Nb(12)-O(36)	1.984(8)	Nb(12)-O(36)	1.978(6)
Nb-O_c	Nb(1)-O(37)	2.391(7)	Nb(1)-O(37)	2.353(6)
	Nb(2)-O(37)	2.469(8)	Nb(2)-O(37)	2.407(6)
	Nb(3)-O(37)	2.401(8)	Nb(3)-O(37)	2.359(5)
	Nb(4)-O(38)	2.414(8)	Nb(4)-O(38)	2.365(6)
	Nb(5)-O(38)	2.461(8)	Nb(5)-O(38)	2.387(6)
	Nb(6)-O(38)	2.414(8)	Nb(6)-O(38)	2.370(6)
	Nb(7)-O(39)	2.412(8)	Nb(7)-O(39)	2.357(6)
	Nb(8)-O(39)	2.461(8)	Nb(8)-O(39)	2.395(6)
	Nb(9)-O(39)	2.376(7)	Nb(9)-O(39)	2.325(6)
	Nb(10)-O(40)	2.381(8)	Nb(10)-O(40)	2.338(5)
	Nb(11)-O(40)	2.434(8)	Nb(11)-O(40)	2.371(5)
	Nb(12)-O(40)	2.457(8)	Nb(12)-O(40)	2.399(5)
T-O_c	Si(1)-O(37)	1.654(8)	Ge(1)-O(37)	1.746(5)
	Si(1)-O(38)	1.643(8)	Ge(1)-O(38)	1.747(5)
	Si(1)-O(39)	1.648(8)	Ge(1)-O(39)	1.764(6)
	Si(1)-O(40)	1.645(8)	Ge(1)-O(40)	1.754(6)

O_t: terminal oxygen; O_b: bridging oxygen; O_c: central oxygen.

Table S6. Selected bond lengths of Sb-O [Å] and bond angles of O-Sb-O [°] for **1**.

	Bond length		Bond angles			
1-Si	Sb(1)-O(6)	2.152(6)	O(6)-Sb(1)-O(7)	76.3(2)	O(6)-Sb(1)-O(6)#1	135.8(3)
	Sb(1)-O(7)	1.992(6)	O(6) -Sb(1)-O(7)#1	76.3(2)	O(7)-Sb(1)-O(7)#1	101.8(3)
1-Ge	Sb(1)-O(6)	2.154(4)	O(6)-Sb(1)-O(7)	76.18(17)	O(6)-Sb(1)-O(6)#3	136.7(2)
	Sb(1)-O(7)	1.993(4)	O(6)-Sb(1)-O(7)#3	76.61(17)	O(7)-Sb(1)-O(7)#3	100.8(3)
1-P	Sb(1)-O(6)	2.153(6)	O(6)-Sb(1)-O(7)	76.2(2)	O(6)-Sb(1)-O(6)#3	135.1(3)
	Sb(1)-O(7)	1.996(5)	O(6)-Sb(1)-(7)#3	76.0(2)	O(7)-Sb(1)-O(7)#3	102.3(3)
1-As	Sb(1)-O(6)	2.162(5)	O(6)-Sb(1)-O(7)	75.90(17)	O(6) -Sb(1)-O(6)#1	135.7(3)
	Sb(1)-O(7)	2.009(5)	O(6)-Sb(1)-O(7)#1	76.31(17)	O(7)-Sb(1)-O(7)#1	100.8(3)
1-V	Sb(1)-O(6)	2.162(5)	O(6)#2-Sb(1)-O(7)	76.07(17)	O(6) -Sb(1)-O(6) #2	136.8(3)
	Sb(1)-O(7)	2.001(5)	O(6)-Sb(1)-O(7)	76.80(18)	O(7)-Sb(1)-O(7)#2	100.8(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1/2,z #2 -y+1/4,x+1/4,-z+1/4 #3 y-1/4,-x+1/4,-z+1/4

Table S7. Selected bond lengths [Å] for **3**.

	3-Si		**3-Ge**	
$Nb\text{-}O_t$	Nb(2)-O(2)	1.752(6)	Nb(2)-O(2)	1.767(5)
	Nb(3)-O(3)	1.764(6)	Nb(3)-O(3)	1.768(5)
	Nb(4)-O(4)	1.754(6)	Nb(4)-O(4)	1.748(5)
	Nb(5)-O(5)	1.741(6)	Nb(5)-O(5)	1.753(5)
	Nb(6)-O(6)	1.773(6)	Nb(6)-O(6)	1.753(5)
	Nb(7)-O(7)	1.772(6)	Nb(7)-O(7)	1.772(5)
	Nb(8)-O(8)	1.762(6)	Nb(8)-O(8)	1.755(5)
	Nb(9)-O(9)	1.762(6)	Nb(9)-O(9)	1.764(5)
	Nb(11)-O(11)	1.743(6)	Nb(11)-O(11)	1.747(5)
	Nb(12)-O(12)	1.772(6)	Nb(12)-O(12)	1.772(4)
$Nb\text{-}O_b$	Nb(1)-O(1)	1.909(5)	Nb(1)-O(1)#1	1.911(4)
	Nb(10)-O(1)#1	1.920(5)	Nb(10)-O(1)	1.926(4)
	Nb(1)-O(13)	1.860(5)	Nb(1)-O(13)	1.862(4)
	Nb(1)-O(15)	2.099(5)	Nb(1)-O(15)	2.103(4)
	Nb(1)-O(30)	2.078(5)	Nb(1)-O(25)	1.855(4)
	Nb(1)-O(25)	1.859(6)	Nb(1)-O(30)	2.094(4)
	Nb(2)-O(13)	2.039(5)	Nb(2)-O(13)	2.060(4)
	Nb(2)-O(14)	2.020(6)	Nb(2)-O(14)	2.013(4)

Nb-O_b	Nb(2)-O(26)	1.964(6)	Nb(2)-O(26)	1.947(5)
	Nb(2)-O(27)	1.938(5)	Nb(2)-O(27)	1.935(4)
	Nb(3)-O(14)	1.904(6)	Nb(3)-O(14)	1.926(4)
	Nb(3)-O(15)	2.070(5)	Nb(3)-O(15)	2.082(4)
	Nb(3)-O(28)	1.881(5)	Nb(3)-O(28)	1.895(4)
	Nb(3)-O(29)	2.138(5)	Nb(3)-O(29)	2.134(4)
	Nb(4)-O(16)	1.918(6)	Nb(4)-O(16)	1.928(4)
	Nb(4)-O(18)	2.120(6)	Nb(4)-O(18)	2.128(4)
	Nb(4)-O(26)	1.894(6)	Nb(4)-O(26)	1.916(5)
	Nb(4)-O(33)	2.112(5)	Nb(4)-O(33)	2.109(4)
	Nb(5)-O(16)	1.953(6)	Nb(5)-O(16)	1.977(4)
	Nb(5)-O(17)	1.957(6)	Nb(5)-O(17)	1.960(4)
	Nb(5)-O(25)	2.028(6)	Nb(5)-O(25)	2.044(4)
	Nb(5)-O(31)	2.042(6)	Nb(5)-O(31)	2.048(4)
	Nb(6)-O(17)	1.922(6)	Nb(6)-O(17)	1.938(4)
	Nb(6)-O(18)	2.095(6)	Nb(6)-O(18)	2.095(4)
	Nb(6)-O(34)	2.111(6)	Nb(6)-O(34)	2.115(4)
	Nb(6)-O(36)	1.903(6)	Nb(6)-O(36)	1.898(5)
	Nb(7)-O(19)	2.082(6)	Nb(7)-O(19)	2.094(4)
	Nb(7)-O(21)	1.908(6)	Nb(7)-O(21)	1.903(5)
	Nb(7)-O(27)	1.900(5)	Nb(7)-O(27)	1.911(4)
	Nb(7)-O(33)	2.096(6)	Nb(7)-O(33)	2.128(4)
	Nb(8)-O(19)	2.082(6)	Nb(8)-O(19)	2.085(5)
	Nb(8)-O(20)	1.896(6)	Nb(8)-O(20)	1.887(5)
	Nb(8)-O(34)	2.143(6)	Nb(8)-O(34)	2.166(5)
	Nb(8)-O(35)	1.904(6)	Nb(8)-O(35)	1.924(4)
	Nb(9)-O(20)	2.001(6)	Nb(9)-O(20)	2.014(5)
	Nb(9)-O(21)	2.007(5)	Nb(9)-O(21)	2.032(5)
	Nb(9)-O(28)	1.972(5)	Nb(9)-O(28)	1.973(4)
	Nb(9)-O(32)	1.945(5)	Nb(9)-O(32)	1.948(5)
	Nb(10)-O(22)	1.853(5)	Nb(10)-O(22)	1.857(4)
	Nb(10)-O(23)	2.097(5)	Nb(10)-O(23)	2.108(4)
	Nb(10)-O(31)	1.839(6)	Nb(10)-O(31)	1.852(4)
	Nb(10)-O(30)	2.114(5)	Nb(10)-O(30)	2.115(4)
	Nb(11)-O(23)	2.065(5)	Nb(11)-O(23)	2.080(4)
	Nb(11)-O(24)	1.923(6)	Nb(11)-O(24)	1.927(4)
	Nb(11)-O(29)	2.133(5)	Nb(11)-O(29)	2.153(4)

	Nb(11)-O(32)	1.902(5)	Nb(11)-O(32)	1.901(5)
	Nb(12)-O(22)	2.060(5)	Nb(12)-O(22)	2.082(4)
	Nb(12)-O(24)	1.959(6)	Nb(12)-O(24)	1.972(5)
	Nb(12)-O(35)	1.941(6)	Nb(12)-O(35)	1.929(4)
	Nb(12)-O(36)	1.962(6)	Nb(12)-O(36)	1.975(5)
$Nb\text{-}O_c$	Nb(1)-O(37)	2.232(5)	Nb(1)-O(37)	2.222(4)
	Nb(2)-O(37)	2.516(5)	Nb(3)-O(37)	2.426(4)
	Nb(3)-O(37)	2.498(5)	Nb(5)-O(38)	2.363(4)
	Nb(4)-O(38)	2.398(5)	Nb(7)-O(39)	2.362(4)
	Nb(5)-O(38)	2.416(5)	Nb(9)-O(39)	2.428(4)
	Nb(6)-O(38)	2.433(5)	Nb(11)-O(40)	2.471(4)
	Nb(7)-O(39)	2.402(5)	Nb(2)-O(37)	2.431(4)
	Nb(8)-O(39)	2.474(5)	Nb(4)-O(38)	2.367(4)
	Nb(9)-O(39)	2.489(5)	Nb(6)-O(38)	2.390(4)
	Nb(10)-O(40)	2.211(5)	Nb(8)-O(39)	2.396(4)
	Nb(11)-O(40)	2.546(5)	Nb(10)-O(40)	2.205(4)
	Nb(12)-O(40)	2.507(5)	Nb(12)-O(40)	2.421(4)
$T\text{-}O_c$	Si(1)-O(37)	1.653(5)	Ge(1)-O(37)	1.769(4)
	Si(1)-O(38)	1.650(5)	Ge(1)-O(38)	1.748(4)
	Si(1)-O(39)	1.637(5)	Ge(1)-O(39)	1.743(4)
	Si(1)-O(40)	1.648(5)	Ge(1)-O(40)	1.759(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2

O_t: terminal oxygen; O_b: bridging oxygen; O_c: central oxygen.

Table S8. Selected bond lengths of Sb-O [Å] for **2**.

2-Si		**2-Ge**	
Sb(1)-O(15)	2.192(8)	Sb(1)-O(15)	2.183(7)
Sb(1)-O(22)	2.161(8)	Sb(1)-O(22)	2.152(6)
Sb(1)-O(25)	2.007(8)	Sb(1)-O(25)	1.993(6)
Sb(1)-O(30)	2.003(8)	Sb(1)-O(30)	1.996(6)
Sb(2)-O(18)	2.186(9)	Sb(2)-O(18)	2.160(6)
Sb(2)-O(20)	2.189(8)	Sb(2)-O(20)	2.169(6)
Sb(2)-O(32)	2.016(8)	Sb(2)-O(32)	1.999(6)
Sb(2)-O(34)	2.002(8)	Sb(2)-O(34)	1.999(6)

Table S9. Selected bond angles of O-Sb-O [°] for **2**.

2-Si		**2-Ge**	
O(15)-Sb(1)-O(22)	137.5(3)	O(15)-Sb(1)-O(22)	138.8(2)
O(15)-Sb(1)-O(25)	77.2(3)	O(15)-Sb(1)-O(25)	76.8(2)
O(15)-Sb(1)-O(30)	76.2(3)	O(15)-Sb(1)-O(30)	76.4(2)
O(22)-Sb(1)-O(25)	77.4(3)	O(22)-Sb(1)-O(25)	77.7(2)
O(22)-Sb(1)-O(30)	77.3(3)	O(22)-Sb(1)-O(30)	77.5(2)
O(25)-Sb(1)-O(30)	103.3(3)	O(25)-Sb(1)-O(30)	101.4(2)
O(18)-Sb(2)-O(20)	137.3(3)	O(18)-Sb(2)-O(20)	138.8(2)
O(18)-Sb(2)-O(32)	76.4(3)	O(18)-Sb(2)-O(32)	77.7(2)
O(18)-Sb(2)-O(34)	76.1(3)	O(18)-Sb(2)-O(34)	76.9(2)
O(20)-Sb(2)-O(32)	77.1(3)	O(20)-Sb(2)-O(32)	76.7(2)
O(20)-Sb(2)-O(34)	77.3(3)	O(20)-Sb(2)-O(34)	77.0(2)
O(32)-Sb(2)-O(34)	102.0(3)	O(32)-Sb(2)-O(34)	101.0(3)

Table S10. Selected bond lengths of Sb-O [Å] for **3**.

3-Si		**3-Ge**	
Sb(1)-O(15)	2.172(5)	Sb(1)-O(15)	2.187(4)
Sb(1)-O(23)	2.146(5)	Sb(1)-O(23)	2.137(4)
Sb(1)-O(29)	2.007(5)	Sb(1)-O(29)	1.996(4)
Sb(1)-O(30)	1.988(5)	Sb(1)-O(30)	1.993(4)
Sb(2)-O(18)	2.135(6)	Sb(2)-O(18)	2.144(4)
Sb(2)-O(19)	2.159(6)	Sb(2)-O(19)	2.176(5)
Sb(2)-O(33)	2.001(6)	Sb(2)-O(33)	1.993(4)
Sb(2)-O(34)	1.983(6)	Sb(2)-O(34)	1.985(4)

Table S11. Selected bond angles of O-Sb-O [°] for **3**.

3-Si		**3-Ge**	
O(15)-Sb(1)-O(23)	136.09(19)	O(15)-Sb(1)-O(23)	137.62(16)
O(15)-Sb(1)-O(29)	76.8(2)	O(15)-Sb(1)-O(29)	76.48(17)
O(15)-Sb(1)-O(30)	75.3(2)	O(15)-Sb(1)-O(30)	75.53(16)
O(23)-Sb(1)-O(29)	76.5(2)	O(23)-Sb(1)-O(29)	77.52(17)
O(23)-Sb(1)-O(30)	76.4(2)	O(23)-Sb(1)-O(30)	76.68(16)
O(29)-Sb(1)-O(30)	101.2(2)	O(29)-Sb(1)-O(30)	99.87(17)
O(18)-Sb(2)-O(19)	136.7(2)	O(18)-Sb(2)-O(19)	138.52(16)
O(18)-Sb(2)-O(33)	77.4(2)	O(18)-Sb(2)-O(33)	77.69(17)
O(18)-Sb(2)-O(34)	77.4(2)	O(18)-Sb(2)-O(34)	77.36(18)
O(19)-Sb(2)-O(33)	75.4(2)	O(19)-Sb(2)-O(33)	76.10(17)
O(19)-Sb(2)-O(34)	76.5(2)	O(19)-Sb(2)-O(34)	76.86(17)
O(33)-Sb(2)-O(34)	102.9(2)	O(33)-Sb(2)-O(34)	101.11(18)

Table S12. The bond valence sum (BVS)[1-2] calculation results of all the V center in **1-V**.

Oxygen Code	**Bond length**	**Bond Valence**
O10	1.724(4)	4.95
O10#1	1.724(4)	
O10#2	1.724(4)	
O10#3	1.724(4)	

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1/2,z #2 -y+1/4,x+1/4,-z+1/4 #3 y-1/4,-x+1/4,-z+1/4

BVS calculation results indicate that the oxidation states of V center in **1-V** is +5.

Table S13. The bond valence sum (BVS) calculation results of Sb centers in **1**.

Compound	1-Si	1-Ge	1-P	1-As	1-V
Bond Valence	3.14	3.12	3.10	3.02	3.05

BVS calculation results indicate that the oxidation states of Sb centers in **1** are +3.

Table S14. The bond valence sum (BVS) calculation results of Sb centers in **2** and **3**.

Compound		2-Si	2-Ge	3-Si	3-Ge
Bond Valence	Sb1	3.01	3.12	3.07	3.08
	Sb2	2.95	3.06	3.16	3.13

BVS calculation results indicate that the oxidation states of Sb centers in **2** and **3** are +3.

1. I. D. Brown and D. Altermatt, *Acta Crystallogr.*, *Sect. B: Struct. Sci.*, 1985, **41**, 244.

2. A. Trzesowska, R. Kruszynski and T. J. Bartczak, *Acta Crystallogr.*, *Sect. B: Struct. Sci.* , 2006, **62**, 745.

Section 4

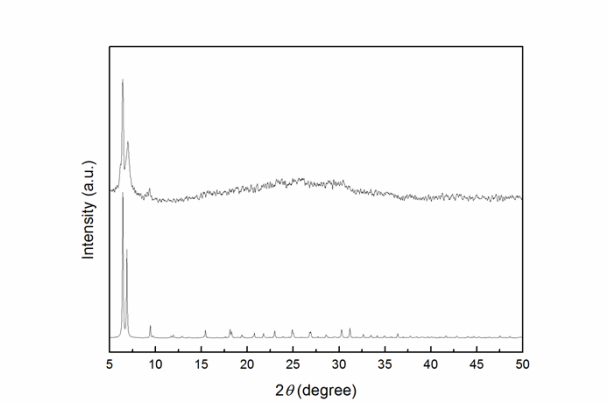

Fig. S5 The XRPD pattern (top) and simulated pattern (bottom) of **1-Si**.

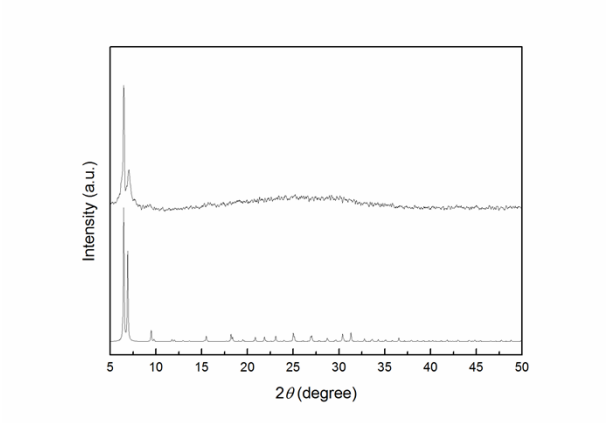

Fig. S6 The XRPD pattern (top) and simulated pattern (bottom) of **1-Ge**.

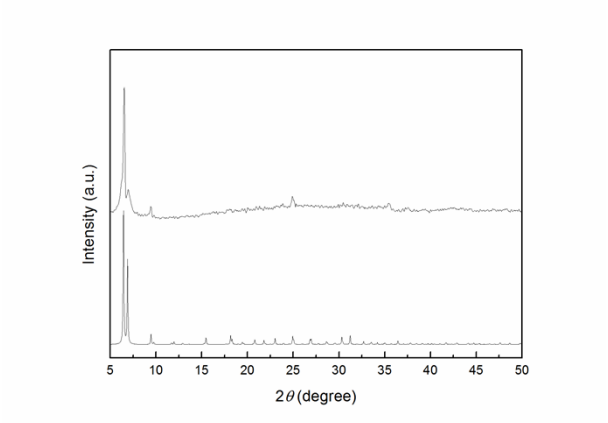

Fig. S7 The XRPD pattern (top) and simulated pattern (bottom) of **1-P**.

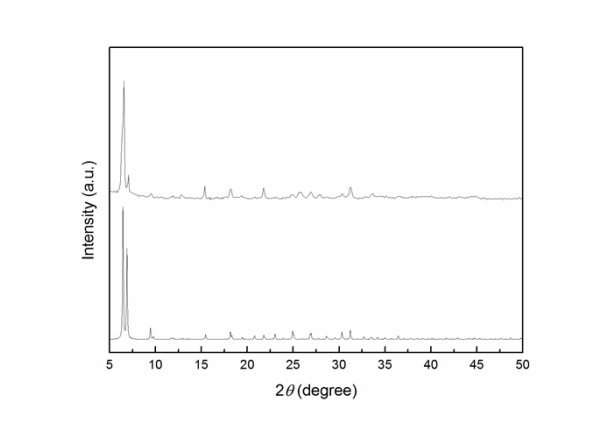

Fig. S8 The XRPD pattern (top) and simulated pattern (bottom) of **1-As**.

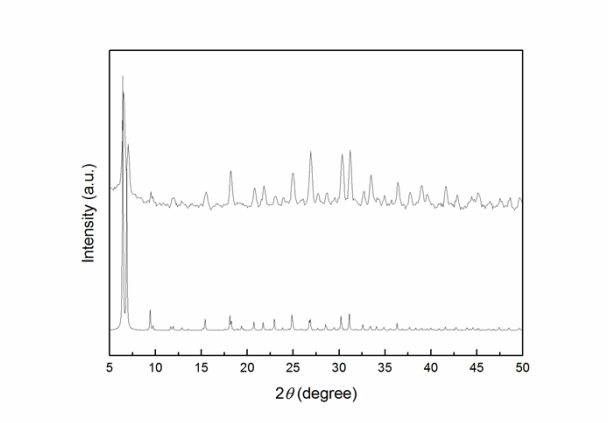

Fig. S9 The XRPD pattern (top) and simulated pattern (bottom) of **1-V**.

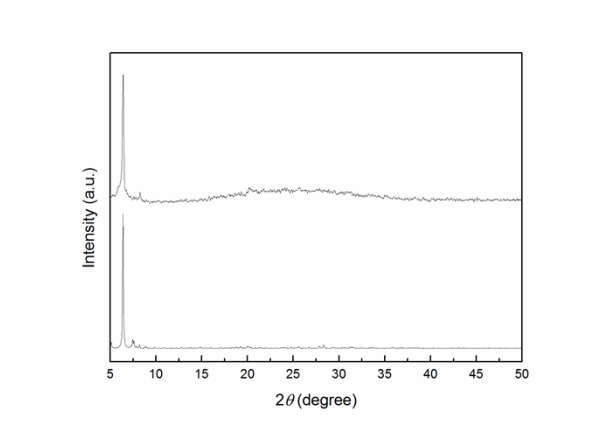

Fig. S10 The XRPD pattern (top) and simulated pattern (bottom) of **2-Si**.

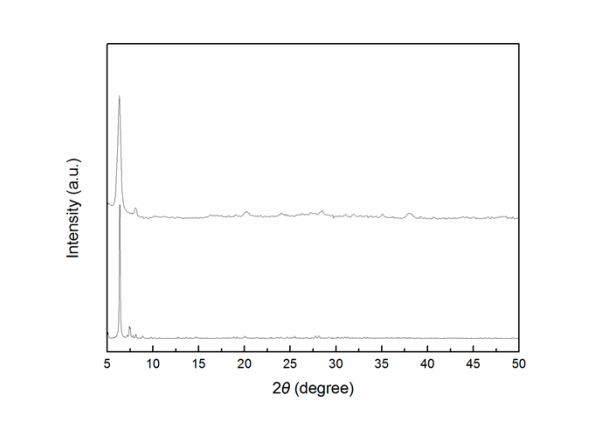

Fig. S11 The XRPD pattern (top) and simulated pattern (bottom) of **2-Ge**.

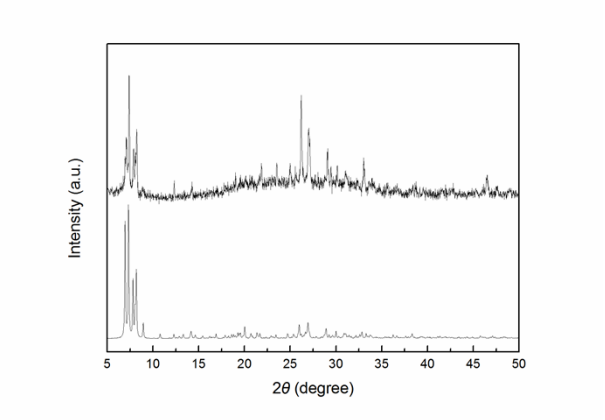

Fig. S12 The XRPD pattern (top) and simulated pattern (bottom) of **3-Si**.

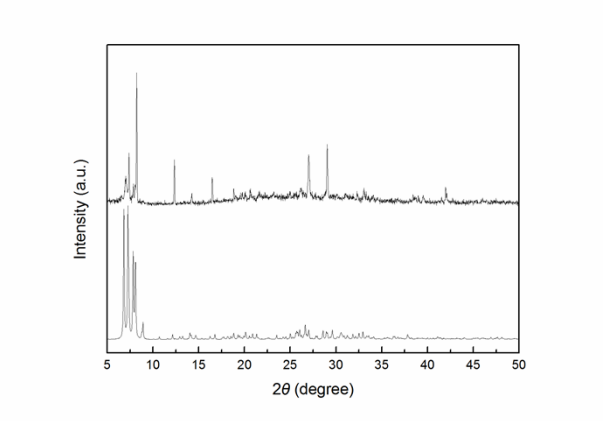

Fig. S13 The XRPD pattern (top) and simulated pattern (bottom) of **3-Ge**.

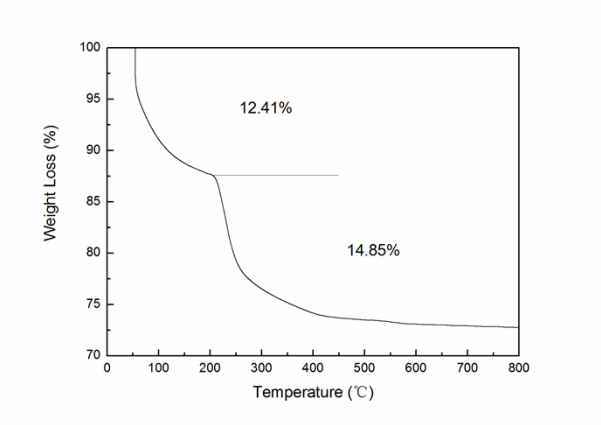

Fig. S14 The TG curve of **1-Si**.

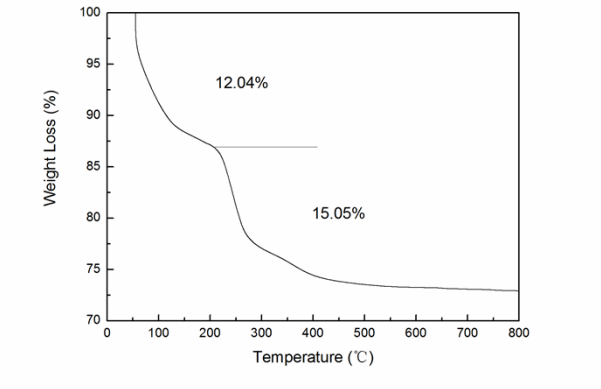

Fig. S15 The TG curve of **1-Ge**.

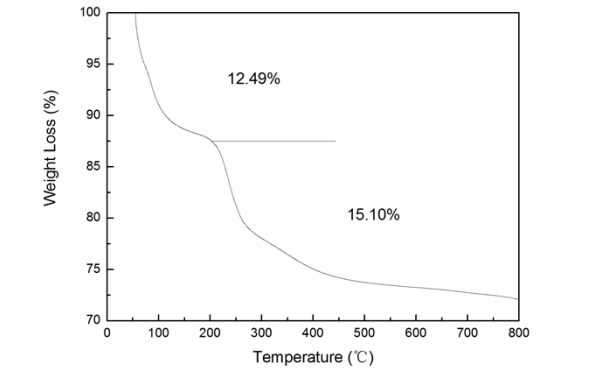

Fig. S16 The TG curve of **1-P**.

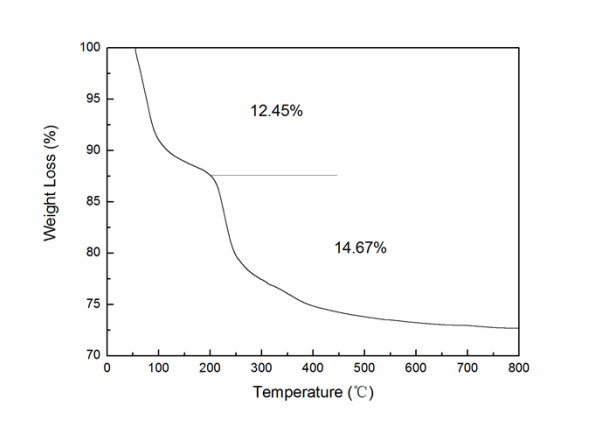

Fig. S17 The TG curve of **1-As**.

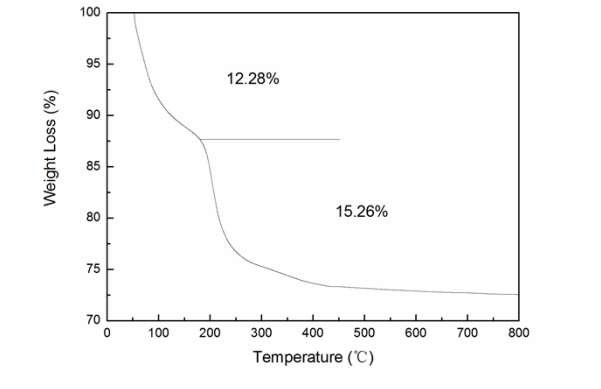

Fig. S18 The TG curve of **1-V**.

TGA studies of 1 The first step weight loss (**1-Si** 12.41%, **1-Ge** 12.04%, **1-P** 12.49%, **1-As** 12.45% and **1-V** 12.28%) in the temperature range *ca*. 30-200 °C, corresponds to the removal of lattice water and the coordination water molecules. (calcd **1-Si** 12.54%, **1-Ge** 12.37%, **1-P** 12.54%, **1-As** 12.36% and **1-V** 12.46%). The second step and the third step are a continuously weight loss (**1-Si** 14.85%, **1-Ge** 15.05%, **1-P** 15.10%, **1-As** 14.67% and **1-V** 15.26%) in the temperature ranges *ca*. 200-300 °C and 300-700 °C, corresponding to the removal of en molecules and the destruction of the polyanions. (calcd en: **1-Si** 15.22%, **1-Ge** 15.00%, **1-P** 15.21%, **1-As** 15.00% and **1-V** 15.11%; destruction of the polyanions: **1-Si** 0.57%, **1-Ge** 0.56%, **1-P** 0.28%, **1-As** 0.28% and **1-V** 0.28%)

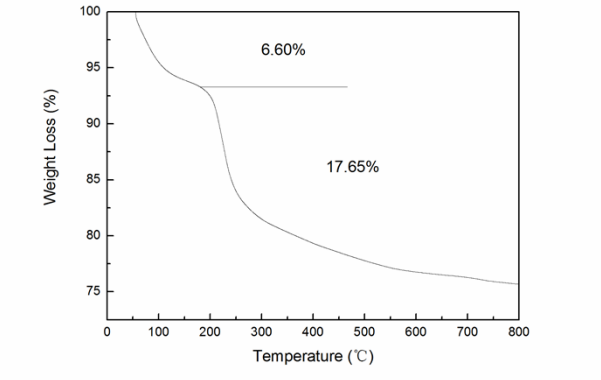

Fig. S19 The TG curve of **2-Si**.

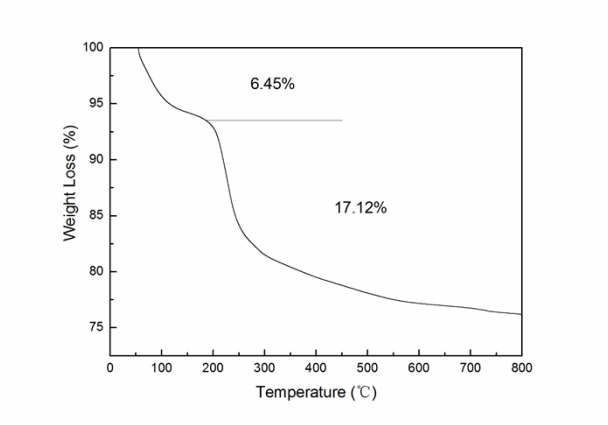

Fig. S20 The TG curve of **2-Ge**.

TGA studies of 2 The first step weight loss (**2-Si** 6.60% and **2-Ge** 6.45%) in the temperature range *ca*. 30-210 °C, corresponds to the removal of lattice water and the water coordination molecules.(calcd **2-Si** 6.49% and **2-Ge** 6.40%). The second step and the third step are a continuously weight loss (**2-Si** 17.65% and **2-Ge** 17.12%) in the temperature ranges *ca*. 210-300 °C and 300-700 °C, corresponding to the removal of en molecules and the destruction of the polyanions. (calcd en: **2-Si** 17.72% and **2-Ge** 17.46%; destruction of the polyanions: **2-Si** 0.15% and **2-Ge** 0.15%)

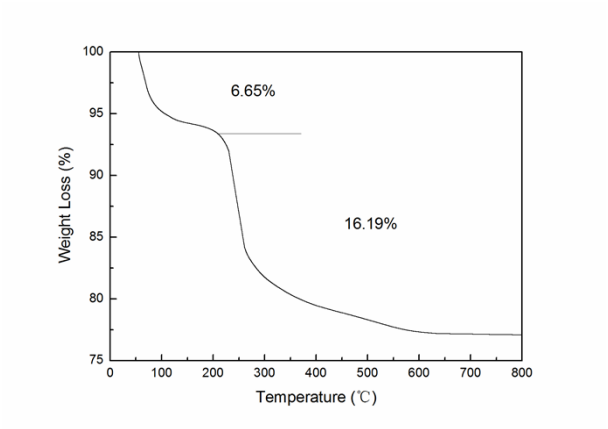

Fig. S21 The TG curve of **3-Si**.

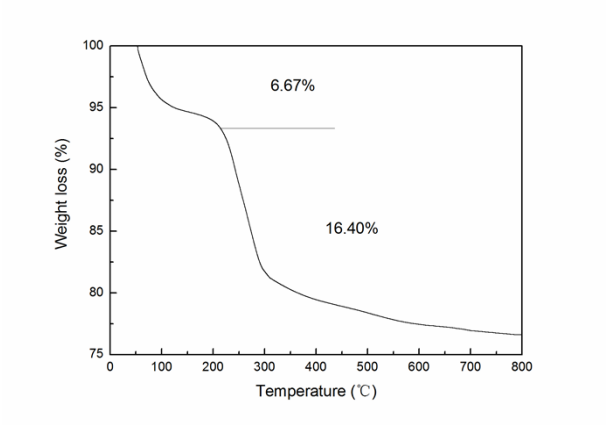

Fig. S22 The TG curve of **3-Ge**.

TGA studies of 3 The first step weight loss (**3-Si** 6.65% and **3-Ge** 6.67%) in the temperature range *ca*. 30-220 °C, corresponds to the removal of lattice water and the coordination water molecules.(calcd **3-Si** 6.73% and **3-Ge** 6.63%). The second step and the third step are a continuously weight loss (**3-Si** 16.19% and **3-Ge** 16.40%) in the temperature ranges *ca*. 220-300 °C and 300-700 °C, corresponding to the removal of en molecules. (calcd en: **3-Si** 16.33% and **3-Ge** 16.09%)

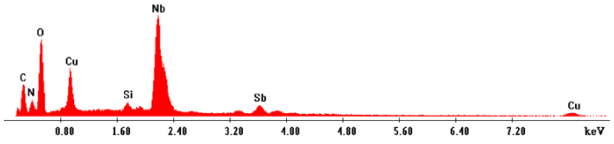

Fig. S23 The EDX spectrum of **1-Si**.

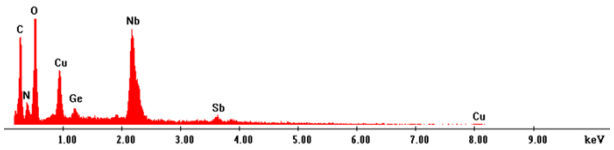

Fig. S24 The EDX spectrum of **1-Ge**.

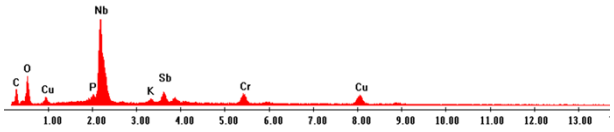

Fig. S25 The EDX spectrum of **1-P**. (Signal of Cr is from depositive conducting film, and signal of K is from contamination of crystals' surface)

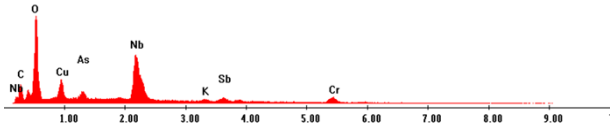

Fig. S26 The EDX spectrum of **1-As**. (Signal of Cr is from depositive conducting film, and signal of K is from contamination of crystals' surface)

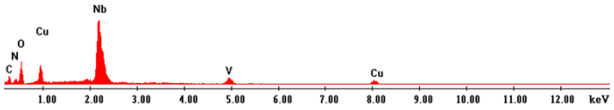

Fig. S27 The EDX spectrum of **1-V**.

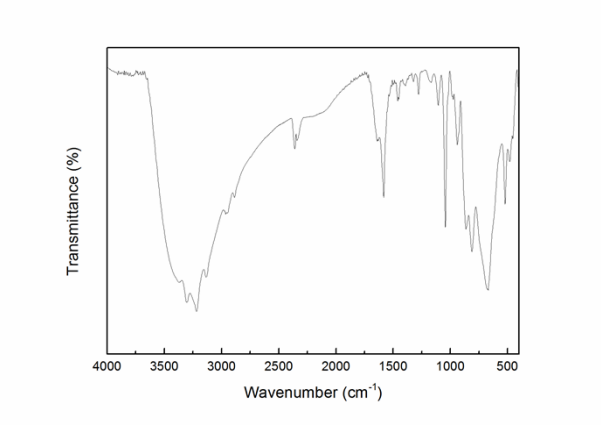

Fig. S28 The FTIR spectrum of **1-Si**.

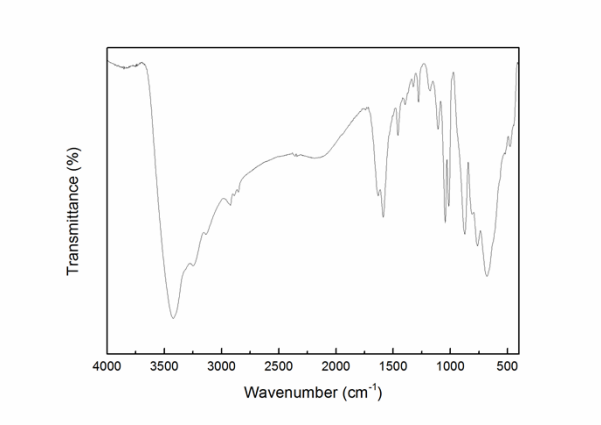

Fig. S29 The FTIR spectrum of **1-Ge**.

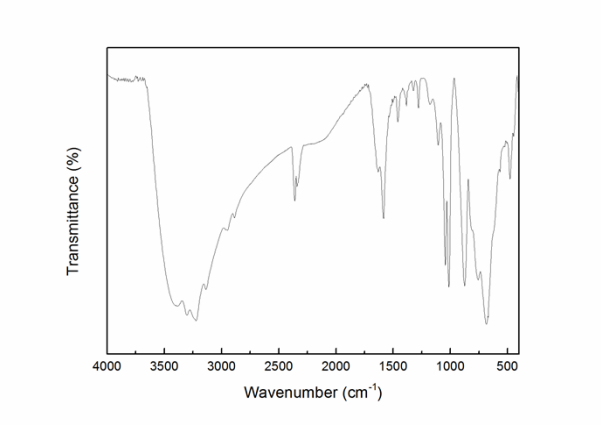

Fig. S30 The FTIR spectrum of **1-P**.

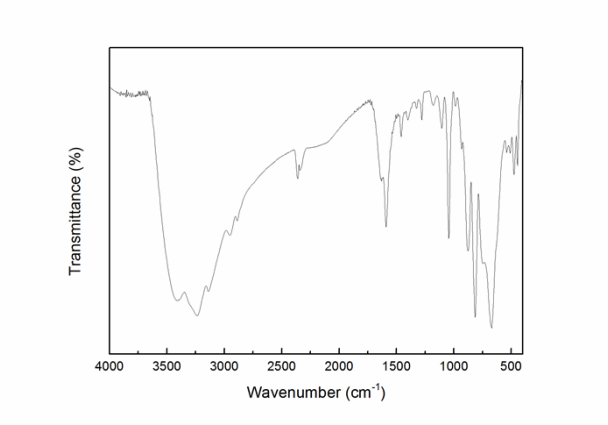

Fig. S31 The FTIR spectrum of **1-As**.

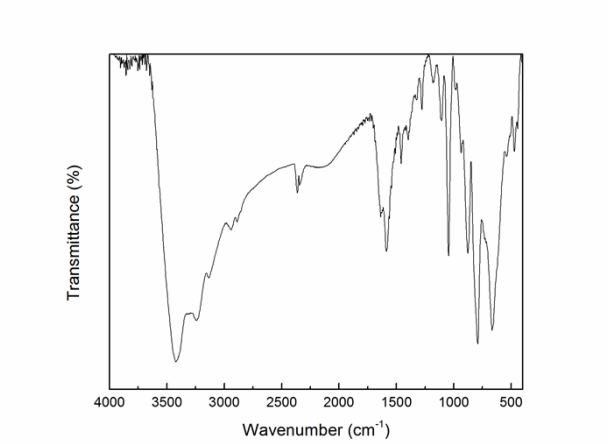

Fig. S32 The FTIR spectrum of **1-V**.

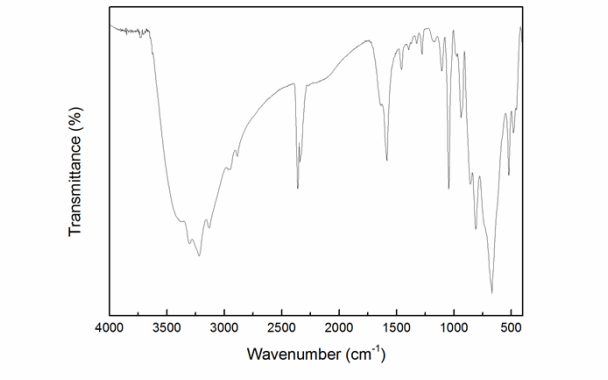

Fig. S33 The FTIR spectrum of **2-Si**.

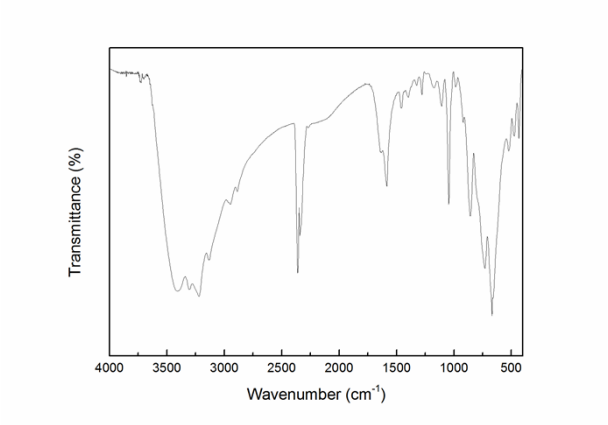

Fig. S34 The FTIR spectrum of **2-Ge**.

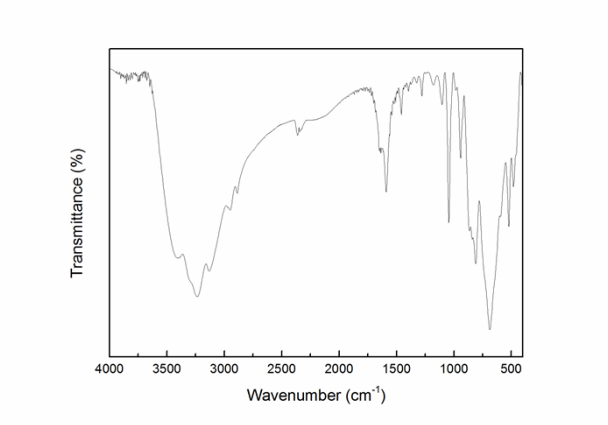

Fig. S35 The FTIR spectrum of **3-Si**.

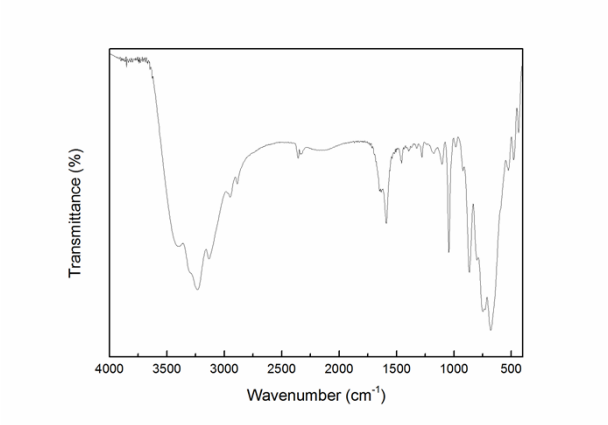

Fig. S36 The FTIR spectrum of **3-Ge**.

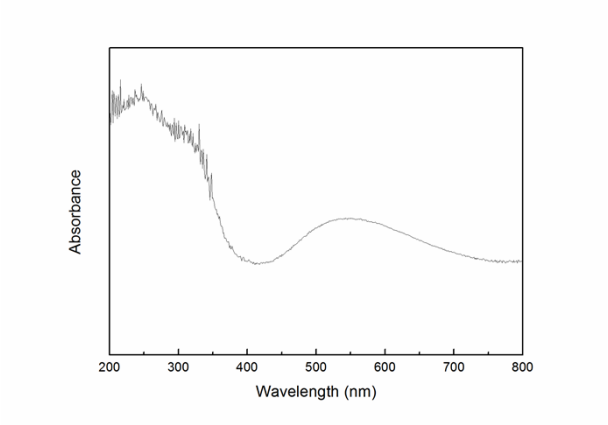

Fig. S37 The solid-state UV-Vis diffuse reflection spectrum of **1-Si**.

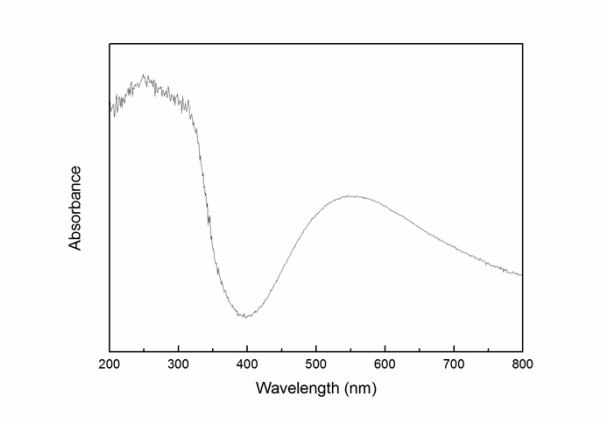

Fig. S38 The solid-state UV-Vis diffuse reflection spectrum of **1-Ge**.

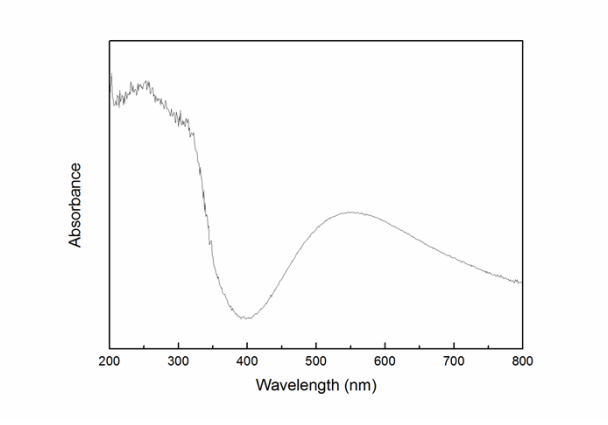

Fig. S39 The solid-state UV-Vis diffuse reflection spectrum of **1-P**.

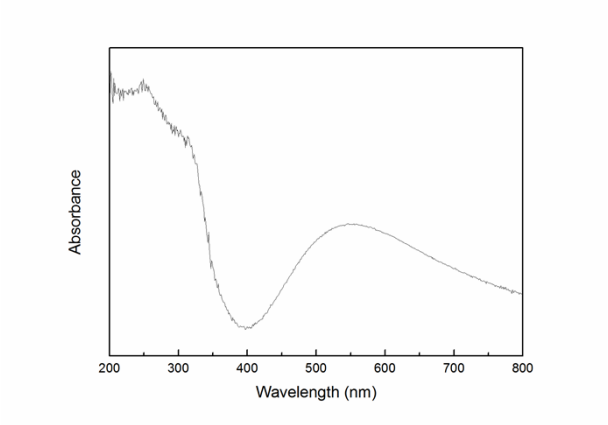

Fig. S40 The solid-state UV-Vis diffuse reflection spectrum of **1-As**.

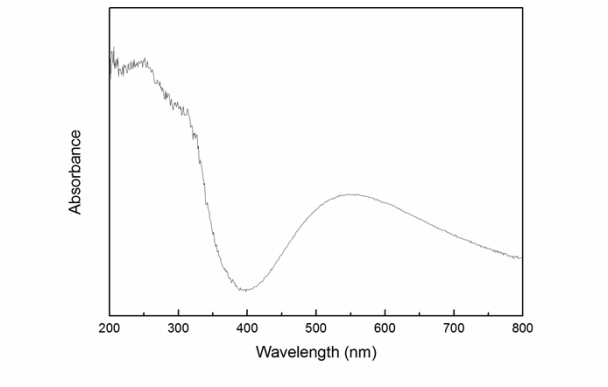

Fig. S41 The solid-state UV-Vis diffuse reflection spectrum of **1-V**.

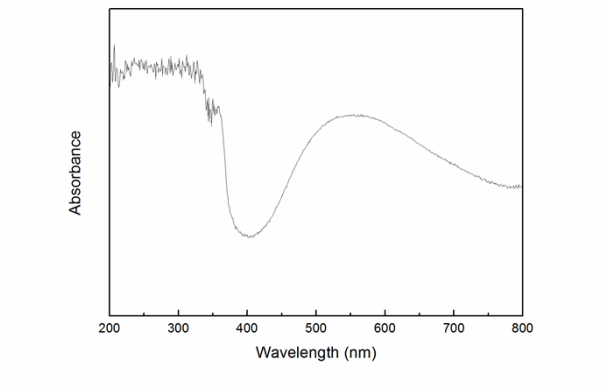

Fig. S42 The solid-state UV-Vis diffuse reflection spectrum of **2-Si**.

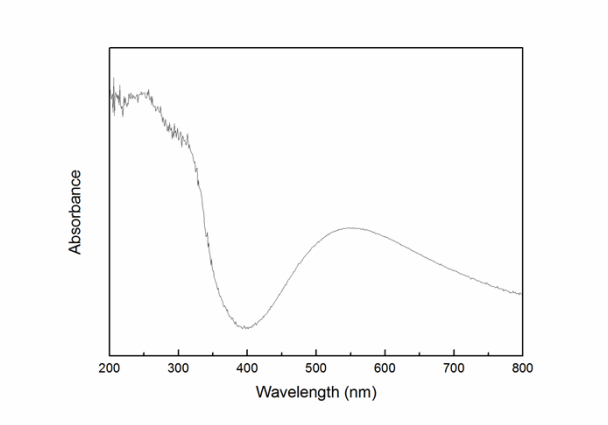

Fig. S43 The solid-state UV-Vis diffuse reflection spectrum of **2-Ge**.

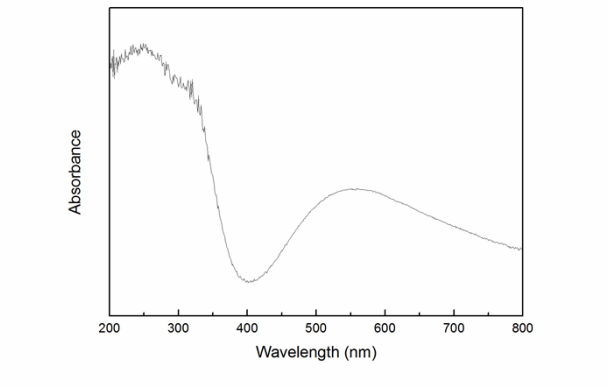

Fig. S44 The solid-state UV-Vis diffuse reflection spectrum of **3-Si**.

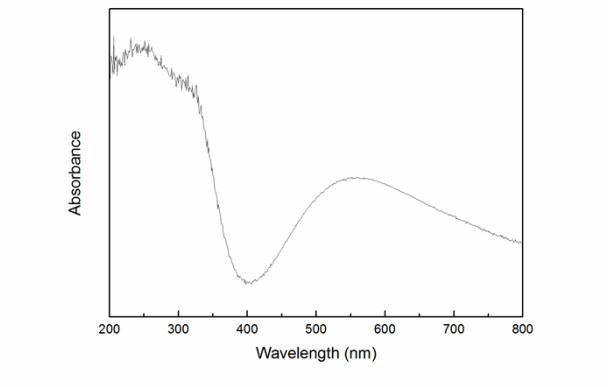

Fig. S45 The solid-state UV-Vis diffuse reflection spectrum of **3-Ge**.