Electronic Supplementary Information (ESI) for:

Complex Cobalt Silicates and Germanates Crystallizing in a Porous Three-Dimensional Framework Structure

Mohammad Usman,[1] Mark D. Smith,[1] Vancho Kocevski,[2] Theodore Besmann,[2] and Hans-Conrad zur Loye,[1*]

[1]*Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States*

[2]*Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina 29208, United States*

**Corresponding Author: E-mail: zurloye@mailbox.sc.edu*

Table S1. Semi-quantitative elemental analyses results.

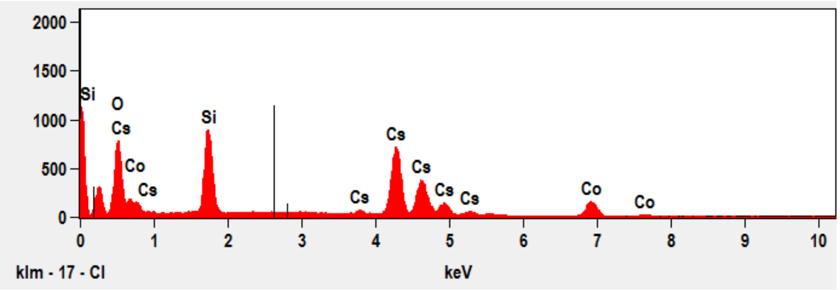
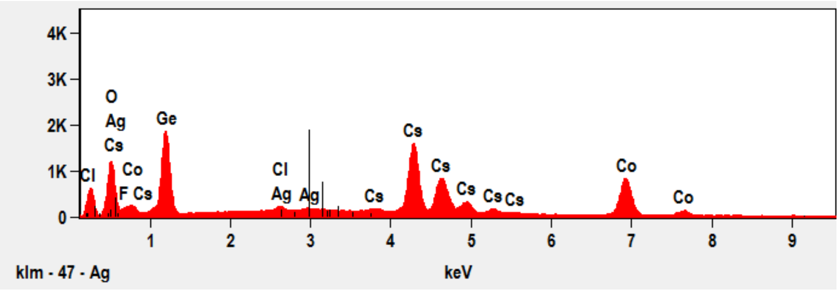
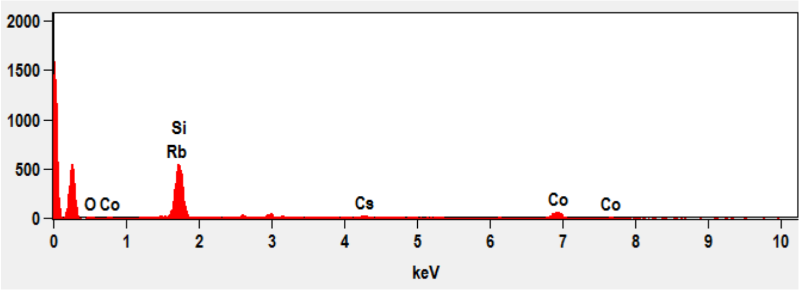
Compound	Atom (%)
$Cs(Co_{0.5}Si_{0.5})SiO_4$ (**1**)	Cs = 15.76, Co = 7.48, Si = 23.29, O = 53.47 
$Cs_{1.29}Co_{0.69}Ge_{1.81}O_5$ (**2**)	Cs = 12.00, Co = 12.40, Ge = 25.04, O = 46.32 
$Cs_{0.86}Rb_{0.14}$ $(Co_{0.5}Si_{0.5})SiO_4$ (**4**)	Cs = 3.24, Rb = 12.55, Co = 19.22, Si = 45.50, O = 19.49 

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $Cs(Co_{0.5}Si_{0.5})SiO_4$ (1). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	Occ	x	y	z	U(eq)
Cs(1)		1915(1)	0	5082(1)	29(1)
Cs(2)		7144(1)	0	3973(1)	27(1)
Co(1)	0.5	3833(4)	0	1169(5)	23(1)
Si(1A)	0.5	3833(4)	0	1169(5)	23(1)
Co(2)	0.5	197(5)	5000	2854(5)	19(1)
Si(2A)	0.5	197(5)	5000	2854(5)	19(1)
Si(1)		131(7)	0	1112(8)	16(2)
Si(2)		3877(8)	5000	2958(7)	17(2)
O(1)		-415(17)	2430(30)	1831(14)	44(4)
O(2)		4566(17)	2630(30)	2149(14)	42(4)
O(3)		1779(9)	0	670(12)	33(2)
O(4)		-989(10)	0	-349(9)	47(3)
O(5)	0.5	-290(18)	4560(40)	4239(10)	38(6)
O(6)		2059(9)	5000	2546(11)	26(2)

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $Cs_{1.29}Co_{0.69}Ge_{1.81}O_5$ (2). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	Occ	**x**	**y**	**z**	**U(eq)**
Ge(1)	0.867	4741(1)	2917(1)	7114(1)	31(1)
Co(1A)	0.133	4741(1)	2917(1)	7114(1)	31(1)
Co(1)	0.85(4)	5000	5000	5000	36(1)
Ge(1A)	0.15(4)	5000	5000	5000	36(1)
O(1)	1	6817(6)	1772(7)	7071(4)	62(1)
O(2)	1	3979(6)	3212(6)	5889(3)	52(1)
O(3)	1	5000	5000	7736(4)	83(3)
Cs(1)	0.181(16)	2120(30)	-42(8)	4876(11)	72(3)
Cs(2)	0.14(2)	2970(50)	-100(14)	4669(9)	81(7)
Cs(3)	0.143(14)	3920(30)	220(9)	4362(12)	81(6)
Cs(4)	0.150(14)	5000	0	4100(20)	158(12)
Cs(5)	0.175(5)	5000	0	2930(14)	142(10)
Cs(6)	0.0164(15)	970(50)	1100(50)	5080(30)	75

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for $Cs_2CoGe_4O_{12}$ (3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	Occ	**x**	**y**	**z**	**U(eq)**
Cs(1)	0.215(2)	2362(5)	4964(3)	2727(2)	63(1)
Cs(2)	0.196(4)	4355(13)	5178(5)	3288(7)	104(4)
Cs(3)	0.025(3)	3460(30)	5030(30)	2985(15)	42(5)
Cs(4)	0.017(3)	4728(19)	5080(30)	3751(19)	26(5)
Cs(5)	0.019(2)	5210(40)	4980(50)	4220(20)	45(7)
Cs(6)	0.019(2)	4820(50)	4930(60)	4719(19)	54(8)
Cs(7)	0.009(2)	2010(80)	6010(90)	2600(50)	61(18)
Ge(1)		5294(1)	2082(1)	384(1)	30(1)
Co(1)		5000	0	2500	31(1)
O(1)		3204(5)	3249(7)	453(4)	52(1)
O(2)		6095(6)	1791(6)	1594(3)	45(1)
O(3)		5000	0	-257(5)	82(3)

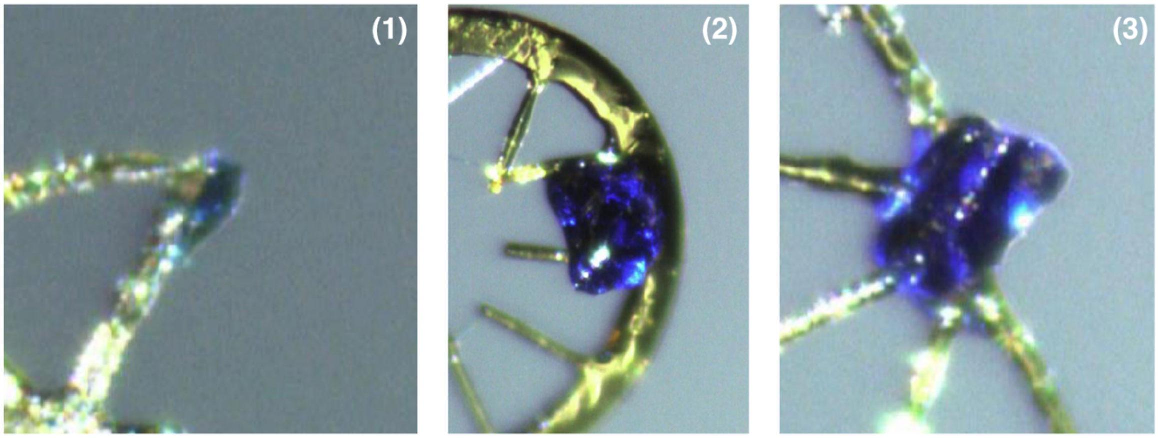


Fig. S1. Single crystal optical images for (**1**) – (**3**).

Relaxed SQSs

$Cs(Co_{0.5}Si_{0.5})Si_2O_4$

```
   1.00000000000000
     8.8325109276669664    0.0000000000000000    0.0118025959073146
     0.0000000000000000    5.4022717927551067    0.0000000000000000
    -0.2442088885052566    0.0000000000000000    9.5018504408105890
   Cs   Co   Si   O
     4     2     6    16
Direct
  0.1782512514440370  0.0000000000000000  0.5136165746923868
  0.6782512514440373  0.5000000000000000  0.0136165746923871
  0.7135077352125299  0.0000000000000000  0.3950099939373720
  0.2135077352125299  0.5000000000000000  0.8950099939373722
  0.3877848514667856  0.0000000000000000  0.1127616047914735
  0.8877848514667853  0.5000000000000000  0.6127615747914783
  0.0268401494242940  0.5000000000000000  0.2702421486397726
  0.5268401404242967  0.0000000000000000  0.7702421786397750
  0.0023677441510898  0.0000000000000000  0.0990721176266453
  0.5023677721510846  0.5000000000000000  0.5990720956266359
  0.3882015356175630  0.5000000000000000  0.2900641700884225
  0.8882015066175637  0.0000000000000000  0.7900641410884239
  0.9539715247653014  0.2497916260863709  0.1911032623097487
  0.9539715247653014  0.7502083439136344  0.1911032623097487
  0.4539714947653057  0.7497916560863656  0.6911032473097437
  0.4539714947653057  0.2502083739136291  0.6911032473097437
  0.4701011502376291  0.2560871139892312  0.2337605339184907
  0.4701011502376291  0.7439128860107693  0.2337605339184907
  0.9701011502376289  0.7560871139892307  0.7337605489184887
  0.9701011502376289  0.2439128860107689  0.7337605489184887
  0.1741285622984525  0.0000000000000000  0.0539557041002071
  0.6741285772984574  0.5000000000000000  0.5539557331002060
  0.8804942810649332  0.0000000000000000  0.9656485346902434
  0.3804943110649360  0.5000000000000000  0.4656485346902440
  0.9889023813811274  0.5000000000000000  0.4321927397247222
  0.4889023813811276  0.0000000000000000  0.9321927397247218
  0.2071762289333212  0.5000000000000000  0.2391288302523101
  0.7071762429333156  0.0000000000000000  0.7391288302523105
```

$Cs_2CoGe_4O_{10}$

```
   1.00000000000000
     7.2156183905354903   -0.0000000053305329    0.0000000000000000
     0.0000000053305329    7.2156183905354903   -0.0000000000000000
     0.0000000000000000    0.0000000000000000   12.7066842368773880
   Cs   Co   Ge   O
     4     2     8    20
```

```
Direct
  0.9769528760034818  0.7465615651029394  0.2309930215637508
  0.7465615651029394  0.0230471239965183  0.7690069784362421
  0.2534384348970607  0.9769528760034818  0.7690069784362421
  0.0230471239965183  0.2534384348970607  0.2309930215637508
  0.5000000000000000  0.0000000000000000  0.2527634197512998
  0.0000000000000000  0.5000000000000000  0.7472365802487072
  0.5479585561418142  0.2052878223579135  0.0375298163916617
  0.4520414438581787  0.7947121926420841  0.0375298163916617
  0.2052878223579135  0.4520414438581787  0.9624701606083400
  0.7947121926420841  0.5479585561418142  0.9624701606083400
  0.0497735524080485  0.7012743734670021  0.5317401366425970
  0.9502264475919515  0.2987256265329908  0.5317401366425970
  0.7012743734670021  0.9502264475919515  0.4682598933573912
  0.2987256265329908  0.0497735524080485  0.4682598933573912
  0.3313875064476045  0.3213766498084040  0.0579923948923132
  0.6686124935523955  0.6786233201916007  0.0579923948923132
  0.3213766498084040  0.6686124935523955  0.9420075971076861
  0.6786233201916007  0.3313875064476045  0.9420075971076861
  0.8368778992086477  0.8222489861384149  0.5595449141834478
  0.1631221007913523  0.1777510438615804  0.5595449141834478
  0.8222489861384149  0.1631221007913523  0.4404550858165522
  0.1777510438615804  0.8368778992086477  0.4404550858165522
  0.6548679157632100  0.1493568113401695  0.1544171749252193
  0.3451320842367900  0.8506431586598352  0.1544171749252193
  0.1493568113401695  0.3451320842367900  0.8455828400747856
  0.8506431586598352  0.6548679157632100  0.8455828400747856
  0.1492207164756115  0.6544742354416524  0.6519902541271051
  0.8507792835243885  0.3455257945583430  0.6519902541271051
  0.6544742354416524  0.8507792835243885  0.3480097458728949
  0.3455257945583430  0.1492207164756115  0.3480097458728949
  0.5000000000000000  0.0000000000000000  0.9610320966159143
  0.0000000000000000  0.5000000000000000  0.0389679293840807
  0.0000000000000000  0.5000000000000000  0.4531619209810009
  0.5000000000000000  0.0000000000000000  0.5468380490190037
```

Detailed Crystallographic Refinement Information for (1) – (3).

(1) crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space groups *I*2, *Im* and *I*2/*m* (*I*-centered monoclinic is the standard setting in this case. The *C*-centered cell is *a* = 12.82 Å, *b* = 5.46 Å, *c* = 8.99 Å, β = 132.9°). *Im* was eventually confirmed by structure solution and was verified with ADDSYM.[1] The asymmetric unit consists of two cesium atoms, two silicon atoms, two mixed sites modeled as 50/50 cobalt/silicon and six unique oxygen atoms. All atoms are located on mirror planes (site 2*a*) except for oxygen atoms O1 and O2, which are located on general positions (site 4*b*). Oxygen O5 displayed a highly elongated displacement ellipsoid if placed on the mirror but refined well if displaced slightly from, and disordered across, the plane. O5 was therefore refined as half-occupied. The cobalt / silicon site mixing was identified by observation of abnormally large displacement parameters when refined as 100% Co. Trial refinements of the cobalt site occupation factors (*sof*s) resulted in significant decreases, to *ca*. 0.73 at each position. This was interpreted as mixing of the lighter atom silicon onto this site instead of the less probable Co/vacancy model. The electroneutral final structure model supports this assignment. Allowing the Co/Si occupancies to refine while constrained to sum to full occupancy gave 50/50 occupation for each site within experimental error (*sof*(Co1/Si1A) = 0.50(3)/0.50(3) and *sof*(Co2/Si2A = 0.51(3)/0.49(3)). These occupancies were therefore fixed at 0.5 each for the final cycles with no change in *R*-values or difference map features. No deviation from full site occupancy was observed for the cesium atoms or for Si1 and Si2. The Co1/Si1A and Co2/Si2A site disorder implies that distances form these sites to oxygen represent weighted averages of Si-O and Co-O contributions. This is reflected also in the larger than normal oxygen displacement ellipsoids, which are a fusion of two different oxygen locations corresponding to the disparate Si-O and Co-O distances. These are unresolvable in the electron density map because of their close proximity, and are accounted for by expanded oxygen displacement parameters. All atoms were refined with anisotropic displacement parameters. The largest residual electron density peak and hole in the final difference map are +0.76 $e^-/Å^3$ and -0.56 $e^-/Å^3$, located 0.88 Å from O3 and 0.40 Å from O4, respectively. The absolute structure (Flack) parameter near convergence was 0.50(7), consistent with the data crystal being an inversion twin. An inversion twinning matrix was included in the final cycles.

The model described above generates an unrealistically short distance of 1.40 Å from site Co2/Si2A to the disordered oxygen O5. Oxygen site O5 is a bridge between the Co2/Si2A and the

Co1/Si1A positions. This is clearly not a genuine distance and is likely an artefact of the extensive disorder in the structure. Various models were attempted to correct this. Curiously, there is no appreciable electron density observed near this site at a more reasonable distance from the mixed Co/Si sites. Restraining the Co2/Si2A and Co1/Si1A distances to more plausible (longer) value gives abnormally large and elongated O5 anisotropic displacement parameters. Synthetic precession images constructed from the full dataset using the Bruker APEX3 program showed no evidence for a different unit cell or lattice centering. For the final model, we have simply retained this O5 position as the best approximate position giving the best data fit.

(2) crystallizes in the tetragonal system. The pattern of systematic absences in the intensity data was inconsistent with the presence of either glide planes or screw axes, leaving eight possible space groups. The space group *I*-4 was identified by the structure solution program XT and confirmed by refinement. The asymmetric unit consists of two unique mixed Co/Ge sites (Ge/Co(1A) on the general position site 8*g*, and Co(1)/Ge(1A) on site 2*a* with -4 site symmetry), three unique oxygen atom sites (O(1) and O(2) on general positions and O(3) on a two-fold axis, site 4*e*) and a disordered distribution of electron density modeled as cesium atoms, most on general positions. The structure is highly disordered, involving all metal sites. Difficulty was encountered in sensibly modeling the disorder within the restraints of crystal electroneutrality. Of the two Co/Ge sites, both refined to less than full occupancy by germanium and to more than full occupancy by cobalt. Both were therefore interpreted as mixed but fully occupied Co/Ge sites. The 8*g* Co/Ge site (Ge(1)/Co(1A)) is predominantly germanium, consistent with the short-observed bond length to oxygen (average 1.75 Å). This site refined to an occupancy ratio of 0.87(3) Ge(1) / 0.13(3) Co(1A). The 2*a* Co/Ge site (Co(1)/Ge(1A)) is predominantly cobalt (distance to oxygen = 1.93 Å x 4), with a refined occupancy ratio of Co(1)/Ge(1A) = 0.85(3)/0.15(3). Physically sensible results were not obtained if the occupancy ratios of both sites were refined simultaneously. The Ge(1)/Co(1A) site occupancy was therefore fixed at the value obtained when only this site was refined (0.867 Ge(1) / 0.133 Co(1A)). Among the Co/Ge-O framework, the Cs cations occupy an essentially continuously disordered array of sites. A total of six Cs atomic positions were modeled, with freely refined occupancies in the range 0.016(2) – 0.18(2). Refinement of the oxygen occupancies showed a decrease from full occupancy only for O(1) and O3, both of which refined to 0.97(2). This is within experimental error of full occupancy, but suggests oxygen vacancies may exist to exactly satisfy charge balance. For the final cycles, all oxygen sites were refined with full occupancy. All Co/Ge and oxygen atoms were refined with anisotropic displacement parameters. Cs(1)-Cs(5) (occupancies 0.14-0.18) were refined anisotropically; Cs(6) (occupancy 0.02) was given a fixed isotropic displacement parameter of 0.075 Å^2. The largest residual electron density peak and hole in the final difference map are +0.46 and -0.37 e$^-$/Å^3, located 0.60 Å from Cs(1) and 2.05 Å from O(1). The absolute structure (Flack) parameter after the final cycle was 0.046(7). Including an inversion twinning matrix did not change the refinement statistics and was therefore omitted. The reliability of the reported structural model is low because of the extensive disorder and the relative similarity of Co and Ge atomic scattering factors. The latter is likely the reason the occupancies of both Co/Ge site could not be refined simultaneously. The approximate nature of the structure model described above is reflected in the large standard uncertainties derived for the occupancy values.

(3) crystallizes in the tetragonal system. The space groups *I*4, *I*-4 and *I*4/*m* were consistent with the pattern of systematic absences in the intensity data. The structure solution program XT returned *I*-4 (No. 82) as the only solution. *I*-4 was subsequently confirmed by structure solution and by checking with ADDSYM.[1] The asymmetric unit consists of one Ge atom, one Co atom, three oxygen atoms and a several disordered electron density peaks which were modeled as partially occupied cesium atoms. Ge1, O1 and O2 and all cesium atoms are all located on positions of general crystallographic symmetry (site 8*g*). Cobalt Co1 is located on a -4 axis (site 2*c*) and oxygen O3 is located on a two-fold axis of rotation (site 4*e*). The cesium atoms are located in channels between the $CoGe_4O_{10}^{2-}$ framework, and appear nearly continuously disordered in the framework channels over multiple sites. Several trial disorder models were refined, the most reasonable of which utilized seven independent, fractionally occupied Cs sites. Two of these dominate (Cs1, occupancy 0.215(2) and Cs2, occupancy 0.196(4)) and were refined anisotropically. The other five (Cs3-Cs7) were refined isotropically, resulting in an occupancy range of 0.025(3) - 0.009(2). Smaller residual peaks (< 0.75 e$^-$/Å^3) remain in this region, but were omitted for refinement stability and because their refined occupancies are effectively zero within error. To achieve crystal charge balance, the total Cs occupancy was constrained to 2 Cs per formula unit. Free refinement gave 2.2 Cs per formula unit, or a +0.2 e- excess. There was only a negligible change in *R*-values upon Cs occupancy constraint. The Ge, Co, and oxygen atoms were refined with anisotropic displacement parameters. No significant deviation from full occupancy was observed for the Ge or Co atoms. The largest residual electron density peak and hole in the final difference map are +0.71 and -0.37 e$^-$/Å^3, located 0.83 Å from Cs1 and 0.96 Å from O2. The absolute structure (Flack) parameter after the final cycle was 0.013(7).

Reference

1. (a) LePage, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264-269. (b) Spek, A. L. *J. Appl. Crystallogr.*, **1988**, *21*, 578-579. (c) Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *46*, C34. (d) **PLATON**: Spek, A.L. *Acta Cryst.,* **2009**, *D65*, 148-155.