Supporting Information for

Deep Eutectic Solvothermal Synthesis of an Open Framework Copper Selenidogermanate with pH-resistant Cs⁺ Ion Exchange Property

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1. Materials and General Methods.

All reagents and solvents employed were commercially available and were used without further purification. Powder X-ray diffraction (XRD) patterns were collected in the angular range of $2\theta = 5-80$ ° on a Rigaku SmartLab 9KW diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) and Energy-dispersive spectroscopy (EDS) were performed on a FEI Quanta FEG 250 scanning electron microscope. FTIR spectra (KBr pellets) were measured on a PerkinElmer Frontier Mid-IR FTIR spectrometer. Solid-state UV/vis reflectance spectra were performed in the wavelength range of $200-2000$ nm using a PerkinElmer Lambda 750 UV/vis spectrophotometer, and a $BaSO_4$ plate was used as a standard (100% reflectance). ^{1}H and ^{13}C NMR spectra of the compound dissolved in mixed $N_2H_4 \cdot H_2O$ (98%)/D_2O were recorded on a Bruker Avance III 400 instrument using 5 mm tubes at room temperature. The concentrations of metal ions in the process of ion exchange were measured by a ThermoFisher iCAP RQ inductively coupled plasma mass spectrometer (ICP-MS). X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer. Elemental analyses on H, C, and N were performed on an Elementar Vario EL cube instrument. **CuGeSe-1** was irradiated at 1.2 kGy/h for a dose of 100 kGy in the ^{60}Co γ irradiation experiment and at 20 kGy/h for two different doses of 100 and 200 kGy in the β irradiation experiment. β irradiation was conducted using electron beams (10 MeV) that were provided by an electron accelerator located in CGN Dasheng Electron Accelerator Co., Ltd., in Jiangsu Province, China.

2. Syntheses.

$[NH_3CH_3]_{0.75}Cu_{1.25}GeSe_3$ (**CuGeSe-1**). A mixture of Cu (0.058 g, 0.9 mmol), Ge (0.104 g, 1.0 mmol), Se (0.236 g, 3.0 mmol), methylamine hydrochloride (0.540 g, 8.0 mmol), N,N'-dimethylurea (1.410 g, 16.0 mmol) and 0.6 mL of $N_2H_4 \cdot H_2O$ (98%) (~12.1 mmol) was sealed in a stainless steel reactor with a 20 mL Teflon liner and heated at 140 °C for 4 days. After cooling to room temperature by natural ventilation, the product was washed with distilled water and then dried in the air. A 0.124 g portion of pure rod-like black crystals of **CuGeSe-1** were collected in a yield of 41 % based on Cu. Anal. Calcd for $C_{0.75}H_{4.5}N_{0.75}Cu_{1.25}GeSe_3$ (412.95): C, 2.18; H, 1.10; N, 2.54. Found: C, 1.80; H, 1.39; N, 2.92.

3. Crystallography

Indexing and data collections of single crystals **CuGeSe-1** and **CuGeSe-1Cs** were performed on a Rigaku XtaLab PRO diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) or Cu Kα radiation ($\lambda = 1.54178$ Å) at 293 K. The absorption corrections were applied using a multiscan technique. The Cu, Ge, Se atoms

in the structure was solved by a direct method using SHELXS-97, and successive Fourier syntheses (SHELXL2014) revealed the remaining atoms.[1] Refinements were conducted by full matrix least squares against $|F|^2$ using all data. All of the Cu, Ge, Se, C and N atoms were refined by anisotropic displacement parameters. The hydrogen atoms around C and N atoms were obtained with idealized geometry. The relevant crystallographic data and structure refinement details are shown in Table S1.

4. Typical Ion-Exchange Experiment

A typical ion exchange experiment was conducted in a batch method at a V/m ratio of 1000 mL/g in a covered 20 mL vial. A quantity of 20 mg of **CuGeSe-1** was added to 20 mL of CsCl aqueous solution with predetermined Cs^+ concentrations, and the mixture was kept at 70 °C with constant stirring for 24 h to reach the adsorption equilibrium. Then the exchanger was isolated by filtration (through filtration paper, Whatman 102) and washed several times with deionized water and dried in air. Single-crystal XRD, XPS, FTIR, UV/vis and EDS mapping measurements were performed on the batch samples obtained from 0.1 M CsCl solution (i.e. **CuGeSe-1Cs**). The Cs:Ge molar ratio of **CuGeSe-1Cs** was determined to be 0.7:1 according to the ICP-MS results, combined with C, H, N elemental analysis and single-crystal XRD data, suggesting an overall formula of $Cs_{0.70}[NH_3CH_3]_{0.05}Cu_{1.25}GeSe_3 \cdot 0.25H_2O$. The filtered solution were diluted by 2% HNO_3 into a suitable scope (below 150 ppb for metal ions) before the concentration of Cs^+ was determined using ICP-MS.

The Cs^+ ion exchange kinetics studies were conducted for various contact time (0-2880 min) in the solution containing ~6 ppm Cs^+. The ion exchange isotherms were studied in solutions with initial concentrations of Cs^+ ranging from 3 to 766 ppm for 24 h contact time.

The individual Cs^+ ion exchange experiments at different pH and salt concentrations were carried out as follows. The required pH values (range from 0 to 13) were achieved by diluting the solution of Cs^+ (600 ppm) with HCl and NaOH solution to ~6 ppm. The experiments were carried out for 24 h contact time, and the pH values of the solution after the ion exchange process were also measured. The effects of coexisting cations were determined by dissolving required amount of NaCl, KCl, $MgCl_2$, $CaCl_2$ in the solution of Cs^+ (~6 ppm), and these experiments were conducted at 70 °C with 24 h contact time.

The Se leaching experiment was conducted in a batch method at a V/m ratio of 1000 mL/g in a covered 20 mL vial. A quantity of 20 mg of **CuGeSe-1** was added to 20 mL of Cs^+ aqueous solution (6 ppm) at pH = 3, 7 and 10, respectively, and the mixture was kept at 70 °C with constant stirring for 24 h. The Se content in filtered solution was determined using ICP-MS (Table S4).

The Cs^+-exchanged product with saturated adsorption, i.e. **CuGeSe-1Cs**, was used

in the elution experiment. The **CuGeSe-1Cs** (20 mg) were soaked in 20 mL of 0.5 M KCl solution at 70 °C with constant stirring for 24 h. Then the solid product was separated by filtration (through filtration paper, Whatman 102) and washed several times with deionized water and dried in air. The product was checked by powder XRD, EDS and elemental mapping.

5. Equations for ion exchange analysis are summarized below:

(1) Pseudo-second-order kinetics model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(1)

Here, k_2 (g·mg^{-1}·min^{-1}) is the pseudo-second-order rate constant of the kinetics model, and the q_t and q_e (mg·g^{-1}) represents the mass of a metal ion adsorbed per unit weight of adsorbent at time t (min) and at equilibrium.

(2) The amount of target ions adsorbed on ion exchangers at equilibrium (q, mg/g):

$$q = \frac{(C_0 - C_e)V}{m}$$

(2)

Here, C_0 (ppm) and C_e (ppm) are the initial and equilibrium concentrations of Cs$^+$ ion, V (mL) is the volume of the test solution, and m (g) is the mass of ion exchanger.

(3) Langmuir-Freundlich isotherm model [2]:

$$q = q_m \frac{(bC_e)^{1/n}}{1 + (bC_e)^{1/n}}$$

(3)

Here, b (L/mg) is the Langmuir constant, q_m (mg/g) is the maximum ion exchange capacity, and n is a parameter characterizing the system heterogeneity.

(4) Distribution coefficient K_d (mL/g):

$$K_d = \frac{V}{m} \frac{(C_0 - C_f)}{C_f}$$

(4)

Here, V (mL) is the volume of the test solution, and m (g) is the mass of ion exchanger, C_0 and C_f (ppm) are the initial and final concentration of the ion.

6. Tables

Table S1. Crystal data for **CuGeSe-1** and **CuGeSe-1Cs**.

Compound	CuGeSe-1	CuGeSe-1Cs
Empirical formula	$C_{0.75}H_{4.50}Cu_{1.25}GeN_{0.75}Se_3$	$C_{0.05}H_{0.80}Cs_{0.70}Cu_{1.25}GeN_{0.05}O_{0.25}Se_3$
Formula weight	412.95	488.04
Crystal system	tetragonal	tetragonal
Space group	$P\bar{4}2_1m$	$P\bar{4}2_1m$
T/K	293(2)	293(2)
λ/Å	0.71073	0.71073
a/Å	12.9345(4)	12.9557(3)
b/Å	12.9345(4)	12.9557(3)
c/Å	8.9057(5)	8.7280(6)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	1489.93(12)	1465.00(12)
Z	8	8
D_c/Mg·m^{-3}	3.682	4.425
μ/mm^{-1}	22.128	25.928
$F(000)$	1476	1698
Measured refls.	6611	6262
Independent refls.	1627	1591
R_{int}	0.0601	0.0397
No. of parameters	75	75
GOF	1.013	1.007
R_1,[a] $wR_2[I > 2\sigma(I)]$	0.0300, 0.0707	0.0273, 0.0616

R_1, wR_2 (all data)	0.0358, 0.0731	0.0295, 0.0622

[a] $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$, $wR_2 = \{\sum w[(Fo)^2-(Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$

Table S2. Selected hydrogen-bonding data for **CuGeSe-1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(1D)···Se(3)#7	0.90	2.69	3.577(15)	166.8
N(2)–H(2A)···Se(3)#8	0.93	3.06	3.77(3)	133.7
N(2)–H(2C)···Se(3)	0.89	3.08	3.77(3)	135.8
C(1)–H(1B)···Se(1)#6	0.97	3.14	4.023(14)	152.5
C(1)–H(1C)···Se(1)	0.95	3.16	4.023(14)	152.6
C(2)–H(2D)···Se(3)#8	0.89	2.92	3.623(17)	137.9
C(2)–H(2E)···Se(3)	0.99	2.77	3.623(17)	144.5
C(2)–H(2E)···Se(4)#2	0.99	2.89	3.43(5)	114.9
C(2)–H(2E)···Se(4)#2	0.99	2.89	3.43(5)	114.9
C(2)–H(2F)···Se(4)#9	1.02	2.93	3.43(5)	110.5

[a]Symmetry codes: #1 -*x*+2, -*y*, *z*; #2 *y*+1, -*x*+1, -*z*+2; #3 -*y*+1, *x*-1, -*z*+2; #4 -*y*+1, *x*-1, -*z*+1; #5 *y*+1, -*x*+1, -*z*+1; #6 *y*+1/2, *x*-1/2, *z*; #7 *x*, *y*, *z*-1; #8 -*x*+2, -*y*+1, *z*; #9 *x*+1/2, -*y*+1/2, -*z*+2.

Table S3. Summary of alkaline metal cation/organic ammonium templated Cu-Ge-Q (Q = S, Se) compounds.

Compounds	Space group	Dimen-sionality	Reactants	Solvent	Yield	Ref.
$CuGe_2S_5(C_2H_5)_4N$	NA	3D	$Cu(Ac)_2 \cdot H_2O$ + GeS_2, 150 °C, 1 d	TEA	55%	[3]
$[(CH_3)_4N]_2Cu_2Ge_4S_{10}$	$I\bar{4}$	3D	Ge + S + $CuCl_2$; 25 °C, 16 h	TMA	NA	[4]
$[Cu_8Ge_6Se_{19}](C_5H_{12}N)_6$	$Im\bar{3}$	3D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + Se; 180 °C, 10 d	Pr	61%	[5]
$[Cu_{16}Ge_{12}S_{36}][Ni(en)_3]_4(en)_xCl_{1.5}$	$Im\bar{3}$	3D	$Ni(Ac)_2 \cdot 4H_2O$ + $CuCl_2 \cdot 2H_2O$ + S + Ge; 180 °C, 8 d	en	57%	
$[Cu_7Ge_4Se_{13}](C_6H_{21}N_4)$	$R3c$	3D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + S; 170 °C, 10 d	TAEA	43%	
$(enH_2)_5[Cu_{16}Ge_6Se_{19}(Se_2)_6] \cdot en$	$Pa\bar{3}$	3D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + S; 170 °C, 6 d	en	67.1%	[6]
$[(CH_3)_2NH_2]_6[Cu_8Ge_6Se_{19}] \cdot 0.25H_2O$	$Im\bar{3}$	3D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + S; 170 °C, 6 d	DMF	37.2%	
$[C_4H_{12}N]_6[(Cu_{0.44}Ge_{0.56}S_{2.23})_4(Ge_4S_8)_3]$	$I\bar{4}_3d$	3D	$Cu(Ac)_2 \cdot H_2O$ + GeS_2; 150 °C, 1 d	TMA	90%	[7]
$[Cu_8Ge_5S_{16}] \cdot x$(solvent)	$Fm\bar{3}c$	3D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + S; 190 °C, 7 d	en	NA	[8]
$A_4Cu_8Ge_3S_{12}$ (A = K, Rb)	$Fm\bar{3}c$	3D	A + Cu + Ge + S; 160 °C, 7 d	en	NA	[9]
$(H_2dab)_2Cu_8Ge_4S_{14} \cdot 2H_2O$	$P2_1/c$	3D	Cu + GeO_2 + S; 165 °C, 7 d	1,4-dab	62%	[10]
$Cu_3GeS_4 \cdot (H_2DAP)_{0.5}$	$Pbca$	2D	Cu + Ge + S; 190 °C, 8 d	1,3-dap	30%	[11]
$Cu_3GeS_4 \cdot (H_2DAP)_{0.5}$	$C2/c$	2D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + S; 190 °C, 8 d	1,3-dap	34%	
$Cu_3GeS_4 \cdot (H_2PR)_{0.5}$	$C2/c$	2D	$Cu(Ac)_2 \cdot H_2O$ + GeO_2 + S; 190 °C, 8 d	AEP	35%	
$[H_4teta]_5[Cu_{40}Ge_{15}S_{60}] \cdot 2.5(teta)$	$Pn\bar{3}n$	3D	CuO + GeO_2 + S; 170 °C, 9 d	teta	45%	[12]
$Na_4Cu_8Ge_3S_{12} \cdot 2H_2O$	$Fm\bar{3}c$	3D	Cu + GeO_2 + S + $NaCO_3$; 160 °C, 7 d	dien	75%	[13]
$(dap)_2(Hdap)_4Cu_8Ge_6S_{18}$	$Im\bar{3}$	3D	Cu + GeO_2 + S; 160 °C, 7 d	dap	23%	

AEP = 1-(2-aminoethyl)piperazinie; DMF = N,N-dimethylformamide; 1,4-dab = 1,4-diaminobutane; TEA = tetraethylammonium; TAEA = tris(2-aminoethyl)amine; TMA = tetramethylammonium; 1,3-dap = 1,3-diaminopropane; teta = triethylenetetramine; dien = diethylenetriamine

Table S4. The concentration (ppm) of Se in the filtrate after the Cs^+ ion-exchange experiments performed at different pH (V = 20 mL, m = 20 mg, 70 °C).

Solutions	Concentration of Se (ppm)
pH = 3	12.58
pH = 7	29.14
pH = 10	35.48

7. Figures
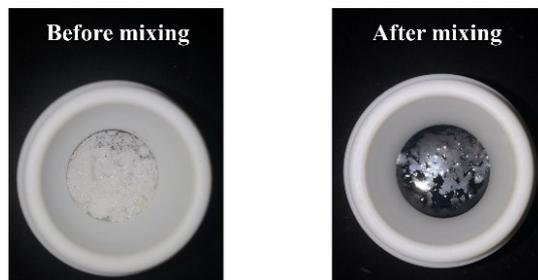
Figure S1. Photographs of the reactants, i.e. Cu, Ge, Se, methylamine hydrochloride, N,N'-dimethylurea (without $N_2H_4 \cdot H_2O$), before and after being mixed. The transforming from bulk solid reactants to a viscous liquid mixture after being stirred indicates the formation of DES.
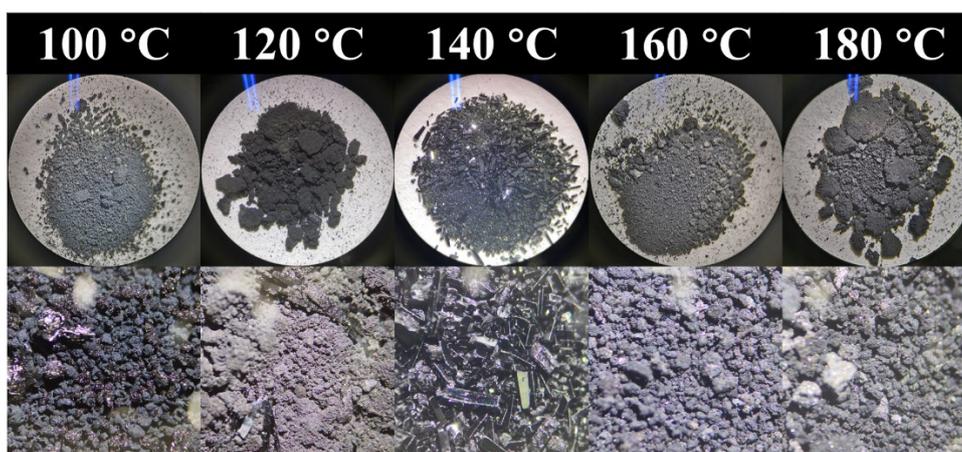
Figure S2. Photographs of the products obtained from the reactions performed at different temperatures. Top line: products washed by distilled water; bottom line: magnified imaging of the products.
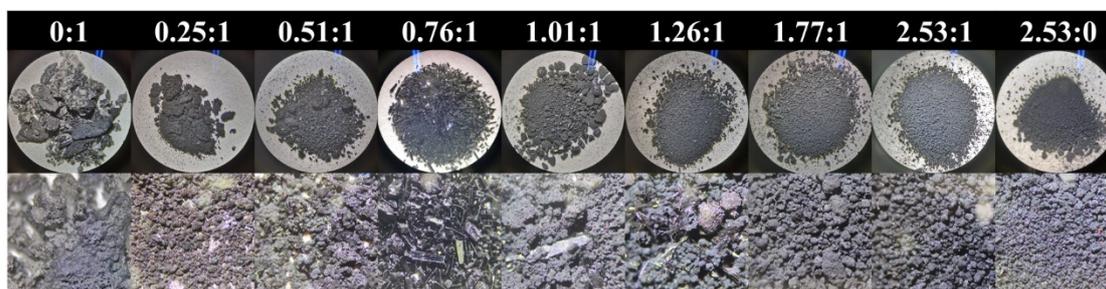
Figure S3. Photographs of the products obtained from the reactions with different $N_2H_4 \cdot H_2O$: N,N'-dimethylurea molar ratios at 140 °C. Top line: products washed by distilled water; bottom line: magnified imaging of the products.
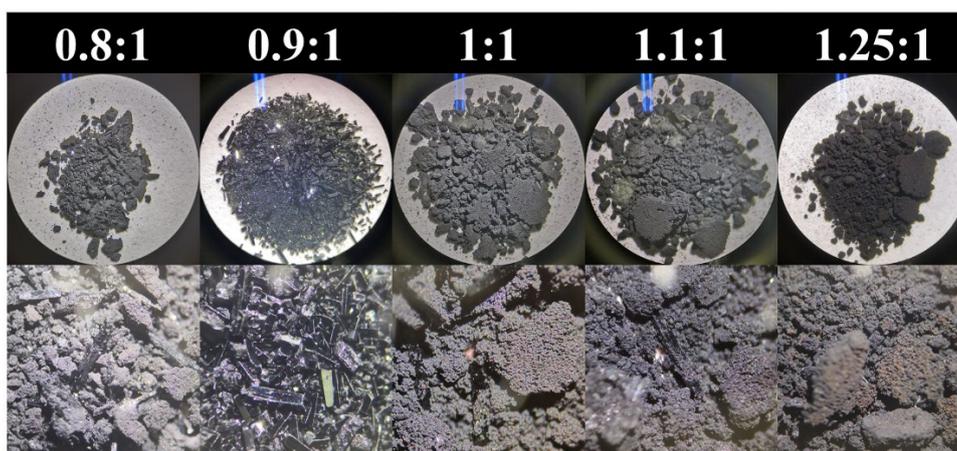
Figure S4. Photographs of the products obtained from the reactions performed at different molar ratio of Cu:Ge. Top line: products washed by distilled water; bottom line: magnified imaging of the products.

$*$ **Cu$_2$Ge$_{1.55}$Se$_3$, PDF-#:36-1198**   **?** **unknown phases**
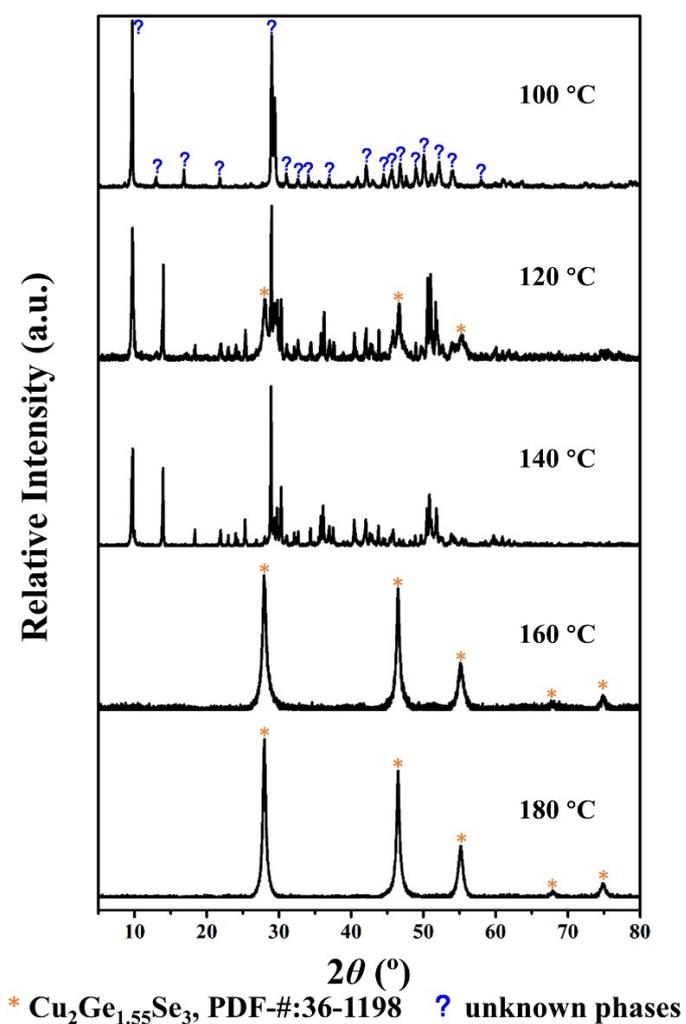
Figure S5. PXRD patterns for the products obtained from the reactions performed at 100-180°C. The molar ratio of N$_2$H$_4$·H$_2$O: N,N'-dimethylurea for all the reactions is 0.76:1.
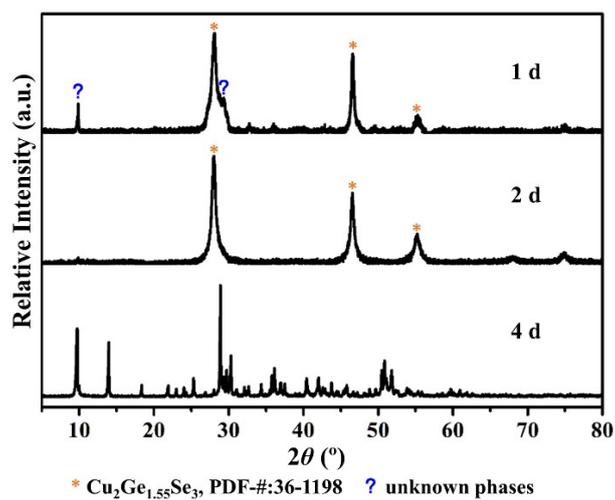
Figure S6. PXRD patterns for the products obtained from the reactions performed at different reaction time at 140°C. The molar ratio of $N_2H_4 \cdot H_2O$:N,N'-dimethylurea for all the reactions is 0.76:1.
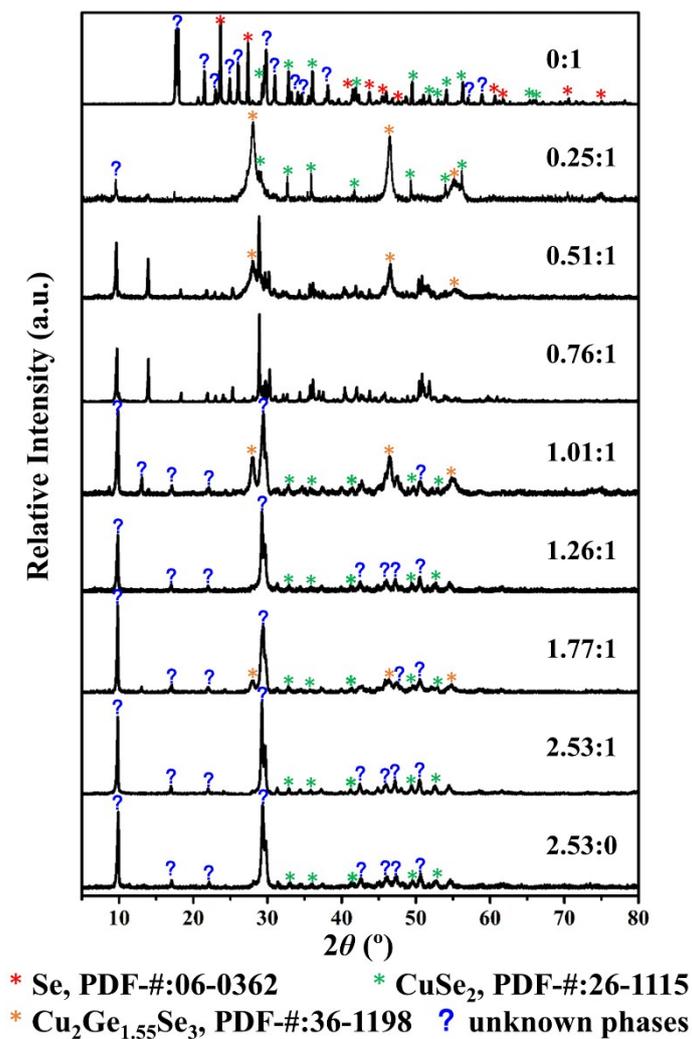
Figure S7. PXRD patterns for the products obtained from the reactions with different $N_2H_4 \cdot H_2O$: N,N'-dimethylurea ratio at 140 °C.
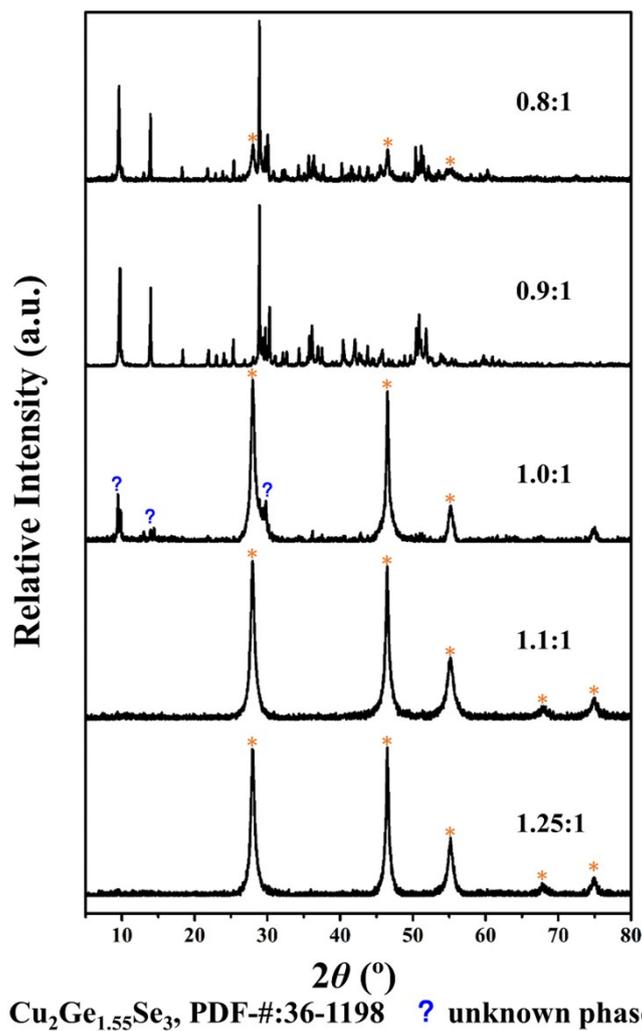
Figure S8. PXRD patterns for the products obtained from the reactions performed at different molar ratio of Cu:Ge range from 0.8:1 to 1.25:1. The molar ratio of $N_2H_4 \cdot H_2O$: N,N'-dimethylurea for all the reactions is 0.76:1.
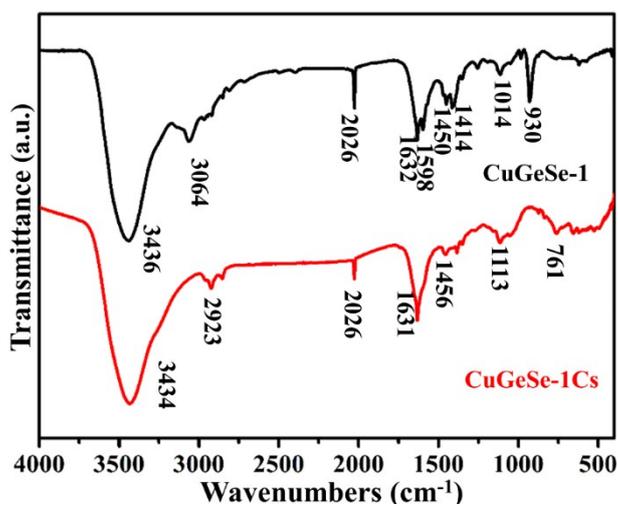
Figure S9. FTIR spectra of **CuGeSe-1** and **CuGeSe-1Cs** measured at room temperature on KBr pellets.
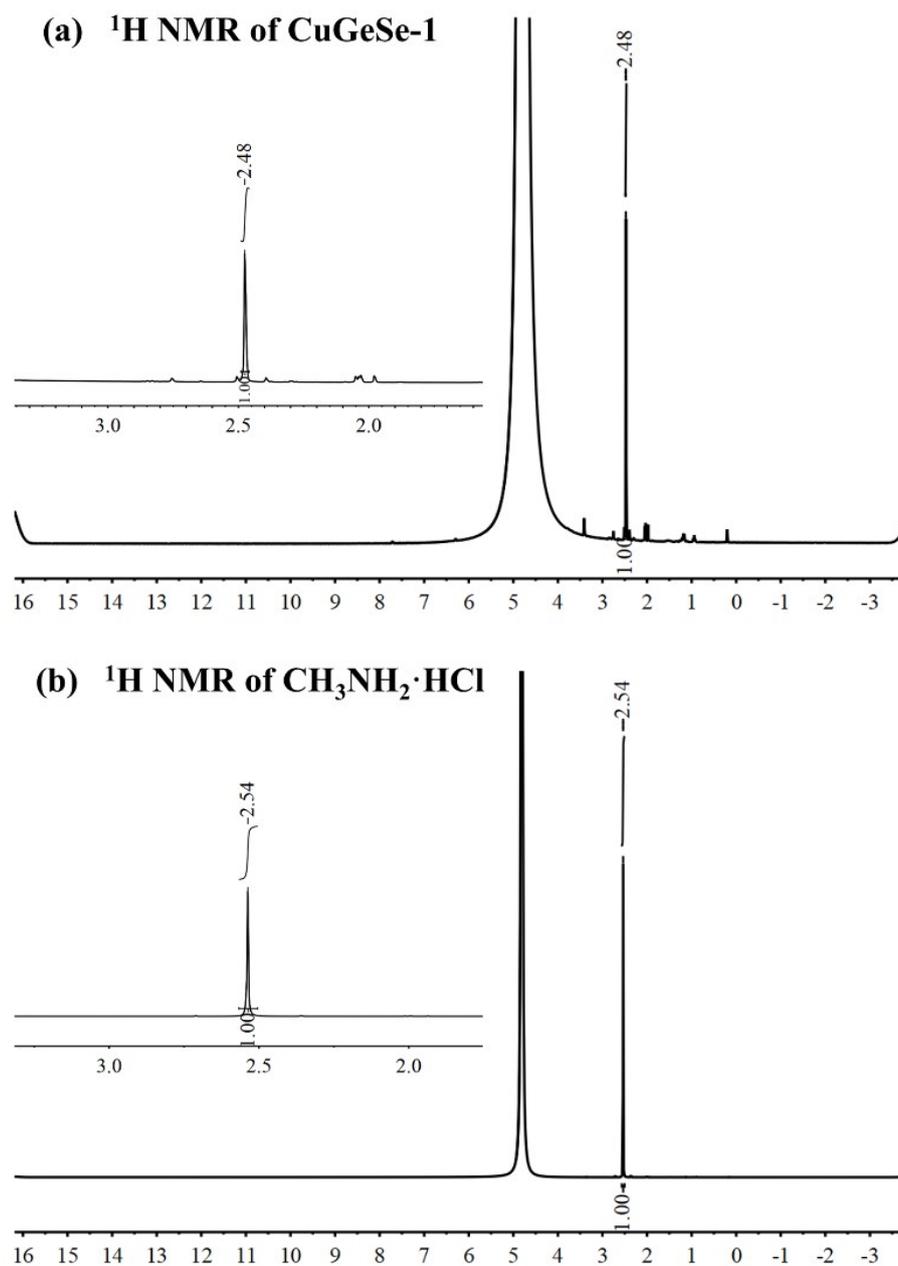
Figure S10. ^{1}H NMR spectra of (a) **CuGeSe-1** and (b) methylamine hydrochloride dissolved in $N_2H_4 \cdot H_2O$ (98%)/D_2O recorded at room temperature.

(a) **¹³C NMR of CuGeSe-1**
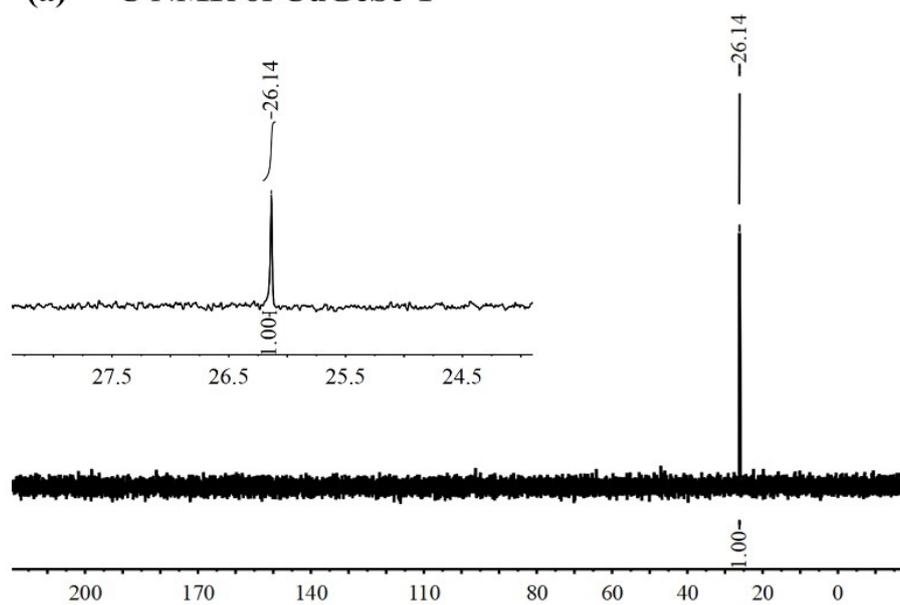
(b) **¹³C NMR of CH₃NH₂·HCl**
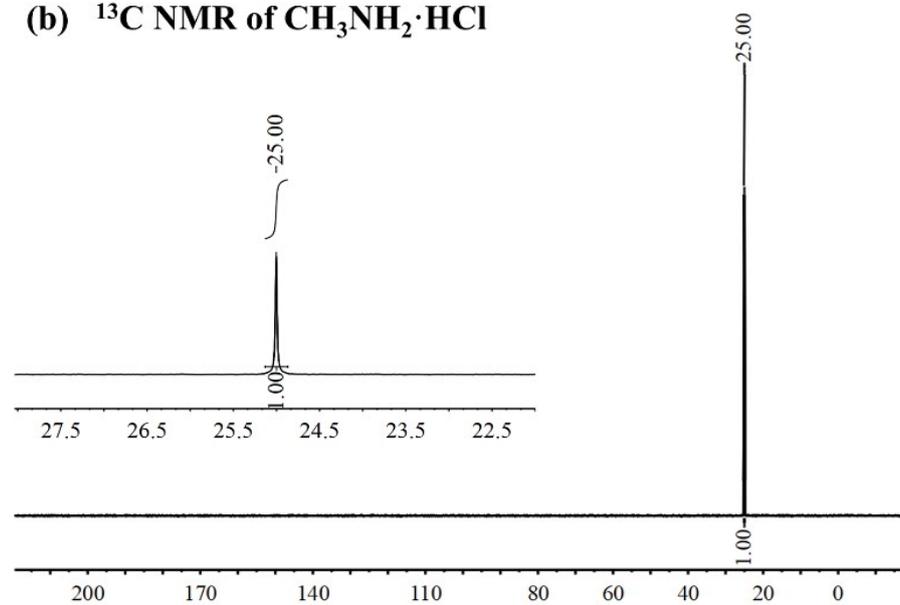
Figure S11. ¹³C NMR spectra of (a) **CuGeSe-1** and (b) methylamine hydrochloride dissolved in $N_2H_4 \cdot H_2O$ (98%)/D_2O recorded at room temperature.
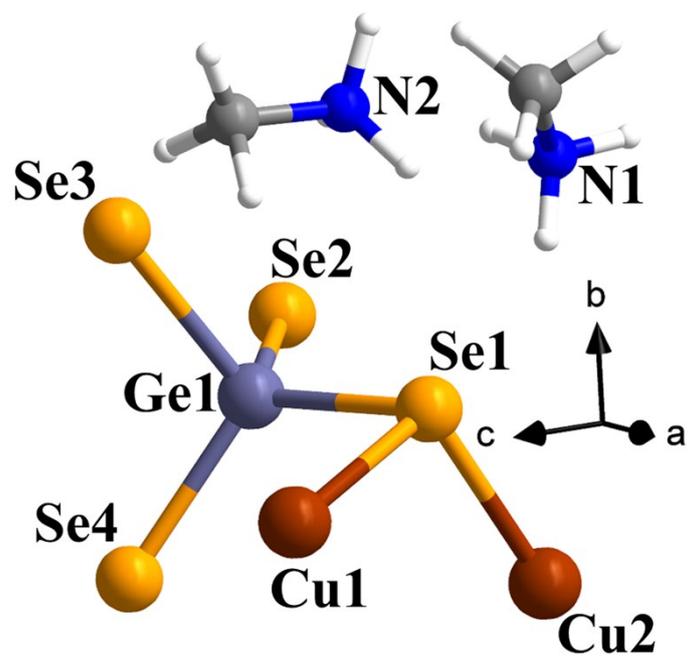
Figure S12. The asymmetric unit of **CuGeSe-1**.
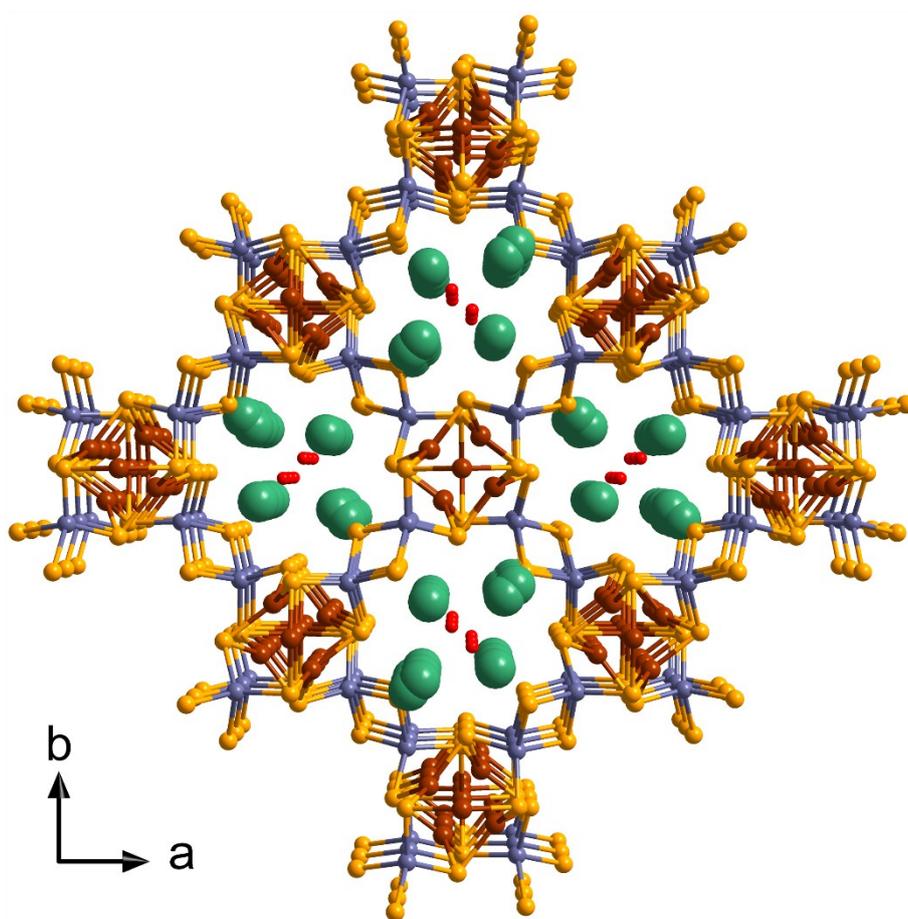
Figure S13. Structure of **CuGeSe-1Cs** viewed along c axis.
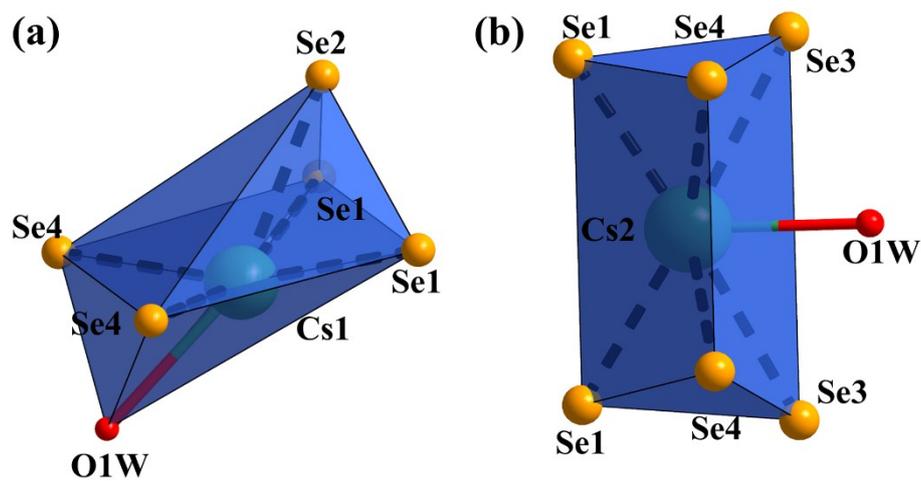
Figure S14. Coordination environments of Cs(1) and Cs(2) in **CuGeSe-1Cs**.
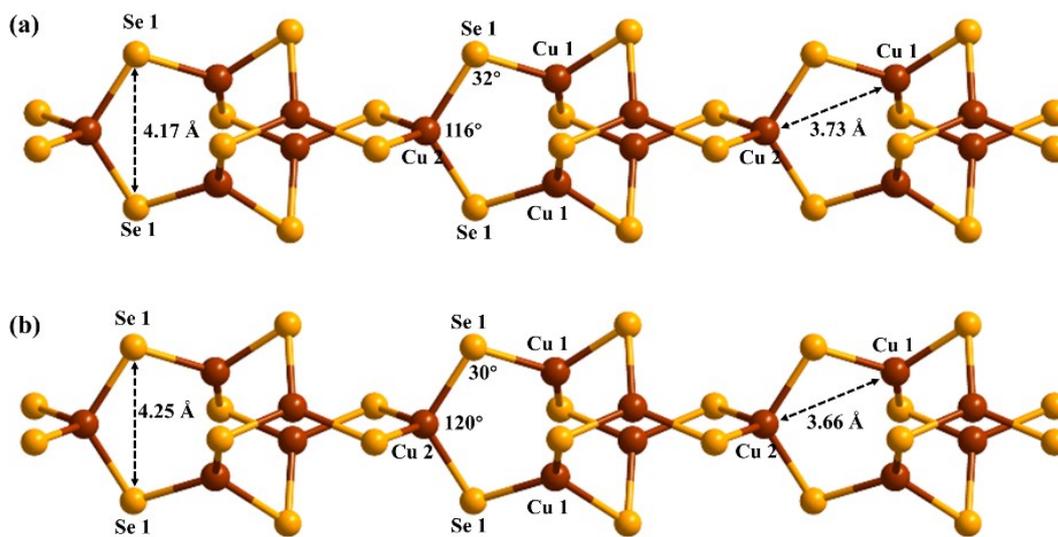
Figure S15. The comparison of the $\{Cu_5Se_8\}_n$ chains in (a) **CuGeSe-1** and (b) **CuGeSe-1Cs**.

element	wt%	atomic%
Cu	21.67	25.20
Ge	18.50	18.82
Se	59.83	55.98
total：	100.00	100.00
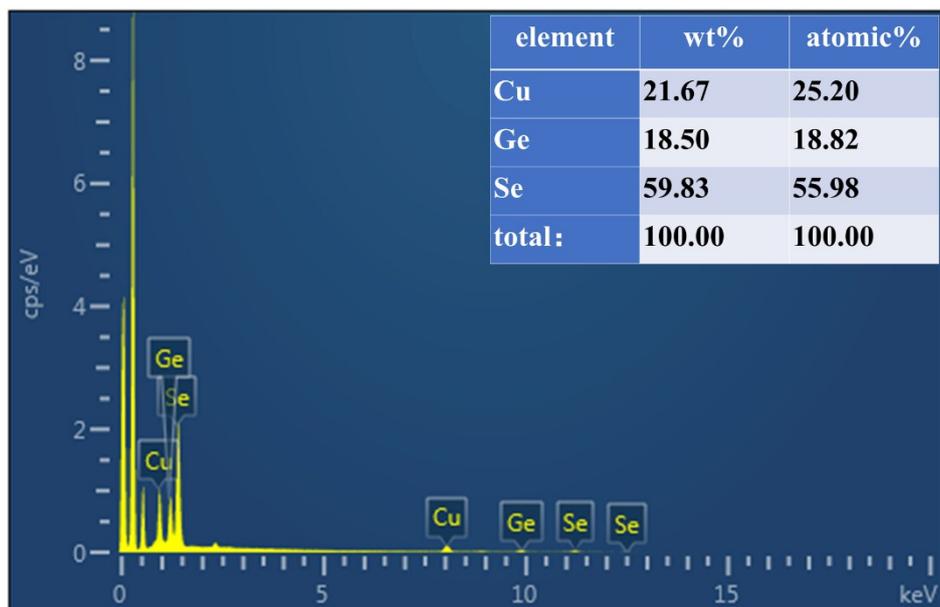
Figure S16. EDS analysis on **CuGeSe-1**.

element	wt%	atomic%
Cu	16.51	20.21
Ge	14.39	15.91
Se	53.72	54.59
Cs	15.38	9.29
total：	100.00	100.00
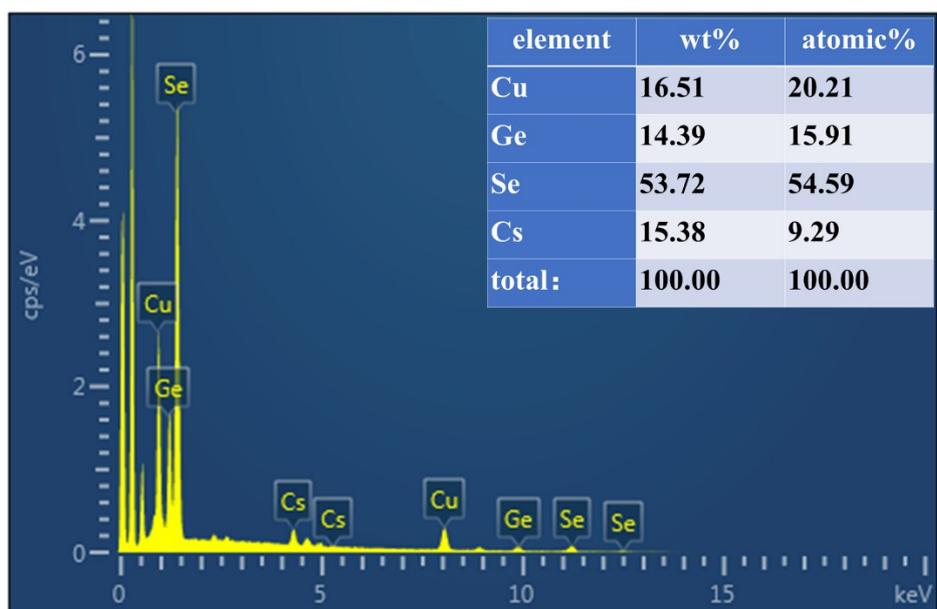
Figure S17. EDS analysis on **CuGeSe-1Cs**.

element	wt%	atomic%
K	5.96	10.68
Cu	21.34	23.53
Ge	17.74	17.11
Se	54.73	48.56
Cs	0.23	0.12
total:	100.00	100.00
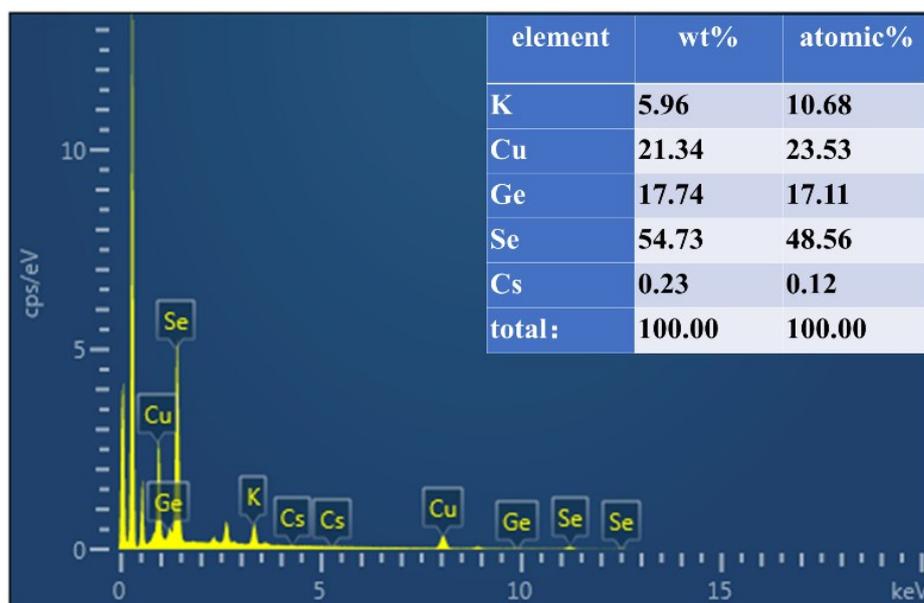
Figure S18. EDS analysis on the eluted exchanger by 0.5M KCl solution.
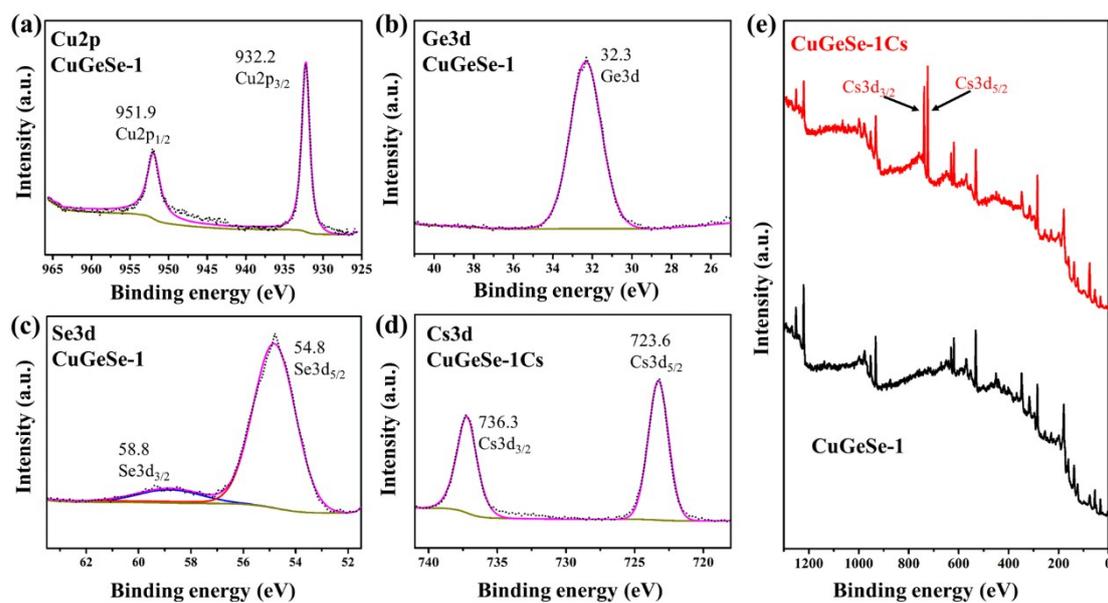
Figure S19. X-ray photoelectron spectra of (a) Cu, (b) Ge, (c) Se for **CuGeSe-1**, and (d) Cs for **CuGeSe-1Cs**. Black dotted and red solid lines represent experimental and overall fitting curves, respectively. (e) Comparisons of experimental survey spectra of the product before (black line) and after (red line) ion exchange.
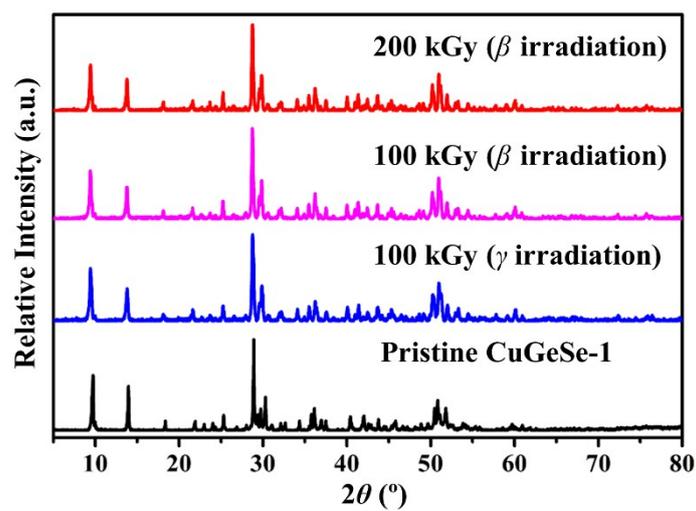
Figure S20. Powder XRD patterns of pristine **CuGeSe-1** and the corresponding samples after β and γ irradiation.
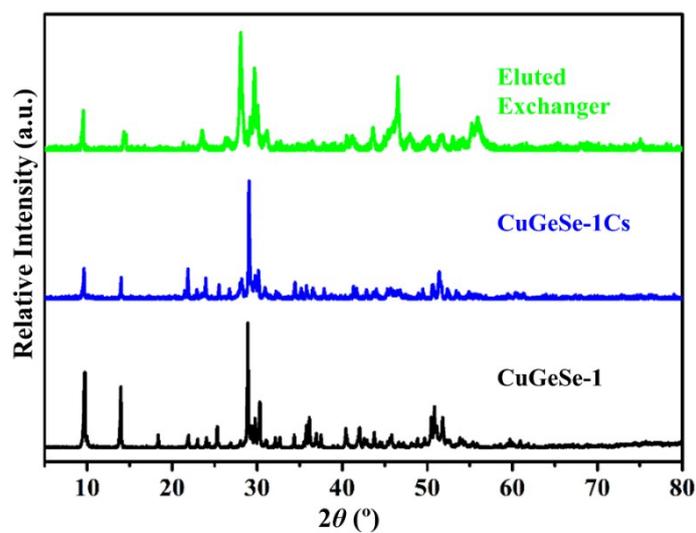
Figure S21. Powder XRD patterns of **CuGeSe-1**, **CuGeSe-1Cs** and eluted exchanger.

References:

[1]   G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr. Sect. A* **2008**, 64, 112-122.

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