# Supporting information

## Crystal Growth of Novel 3D Skeleton Uranyl Germanium Complexes: Influence of Synthetic Conditions to Crystal Structures

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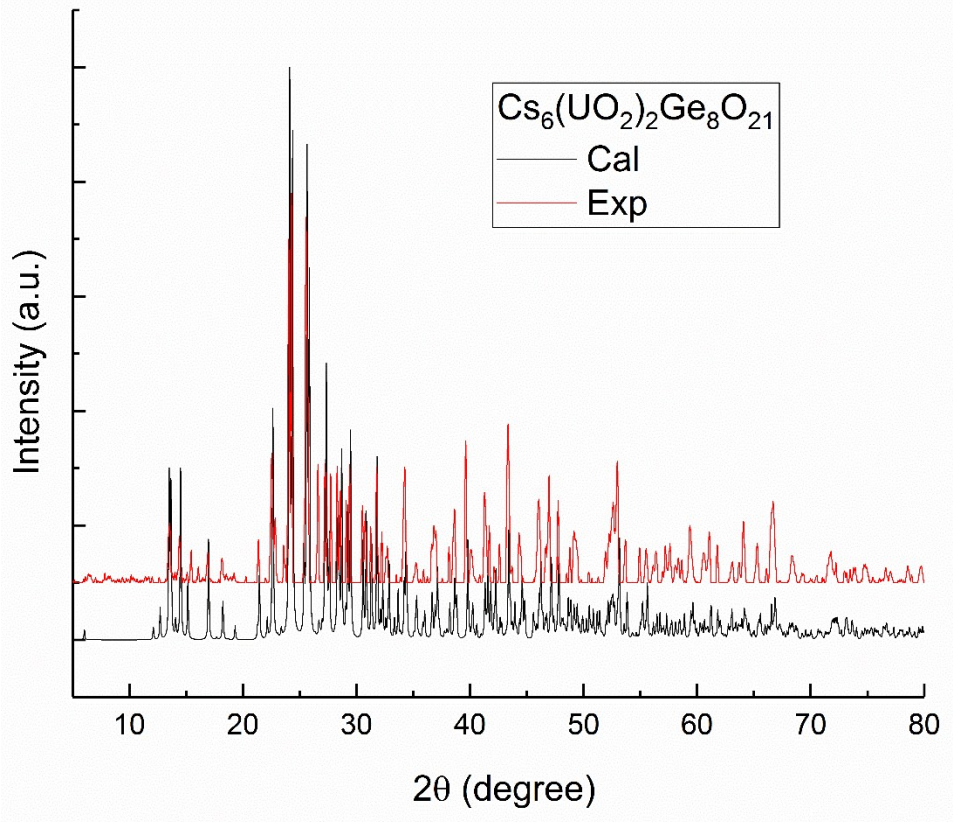


**Figure S1.** The theoretical (black line) and experimental (red line) powder diffraction patterns of $Cs_6(UO_2)_2Ge_8O_{21}$. The theoretical diffraction patterns were calculated using *Mercury* software (version 3.8).[1]

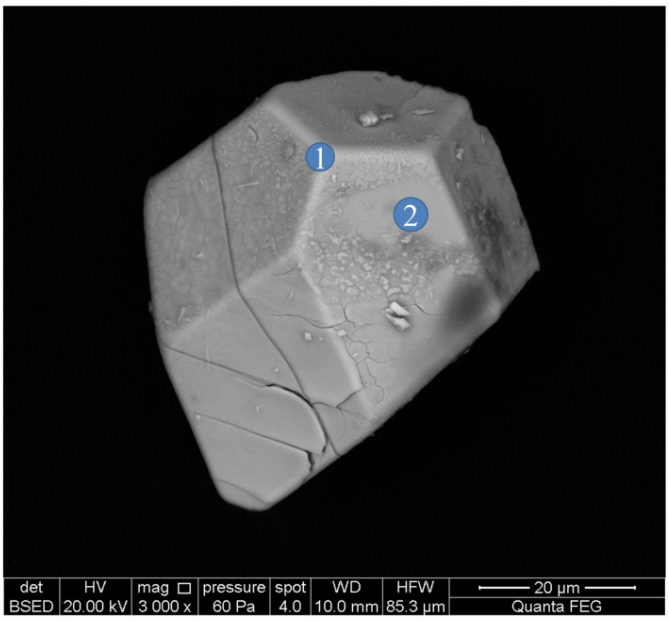


**Figure S2(a)**. EDS analysis for $K_8BrF(UO_2)_3(Ge_2O_7)_2$.

**Table S1 (a)**. Atom ratio of $K_8BrF(UO_2)_3(Ge_2O_7)_2$. (U is keep as 3)

| | U | Ge | K | Br | F |
|---|---|---|---|---|---|
| Point1 | 3 | 4.29 | 7.71 | 1.03 | 0.56 |
| Point2 | 3 | 4.13 | 6.20 | 1.16 | 0.82 |
| Average | 3 | 4.21 | 7.00 | 1.10 | 0.69 |

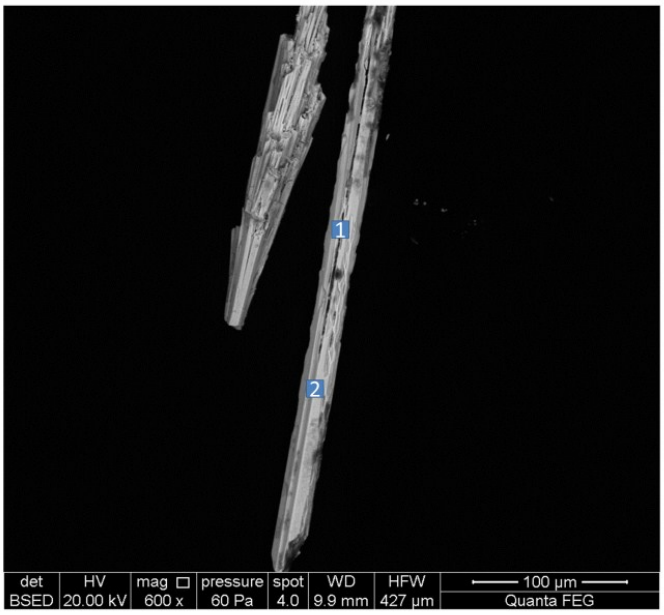


**Figure S2(b)**. EDS analysis for $Rb_6(UO_2)_3(Ge_2O_7)_2{\cdot}0.5H_2O$.

**Table S1 (b)**. Atom ratio of $Rb_6(UO_2)_3(Ge_2O_7)_2{\cdot}0.5H_2O$. (U is keep as 3)

| | U | Ge | Rb |
|---|---|---|---|
| Point1 | 3 | 4.43 | 8.56 |
| Point2 | 3 | 4.67 | 6.16 |
| Average | 3 | 4.55 | 7.36 |

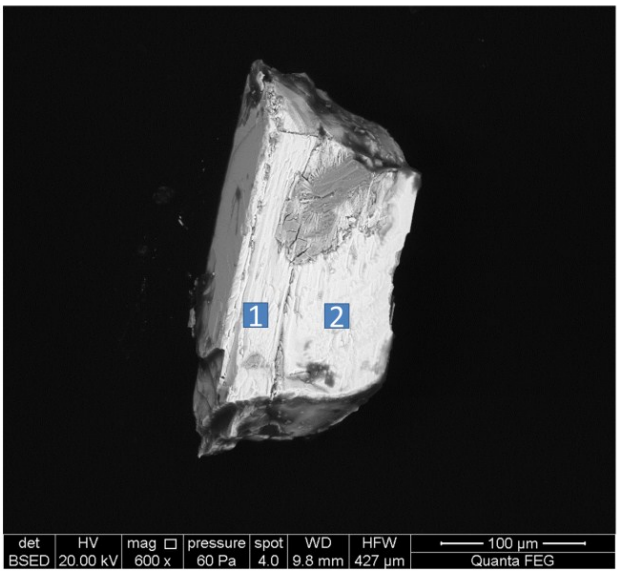


**Figure S2(c)**. EDS analysis for $Cs_6(UO_2)_2Ge_8O_{21}$.

**Table S1(c)**. Atom ratio of $Cs_6(UO_2)_2Ge_8O_{21}$. (U is keep as 2)

| | U | Ge | Cs |
|---|---|---|---|
| Point1 | 2 | 9.42 | 6.92 |
| Point2 | 2 | 8.72 | 6.30 |
| Average | 2 | 9.07 | 6.61 |

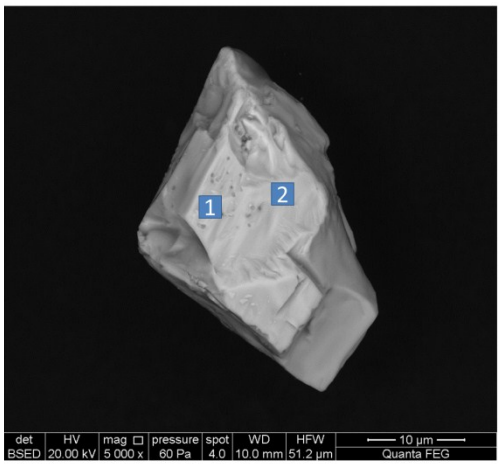


**Figure S2(d)**. EDS analysis for $Rb_2(UO_2)_3(GeO_4)_2$.

**Table S1(d)**. Atom ratio of $Rb_2(UO_2)_3(GeO_4)_2$. (U is keep as 3)

| | U | Ge | Rb |
|---|---|---|---|
| Point1 | 3 | 2.28 | 2.45 |
| Point2 | 3 | 2.28 | 2.35 |
| Average | 3 | 2.28 | 2.40 |

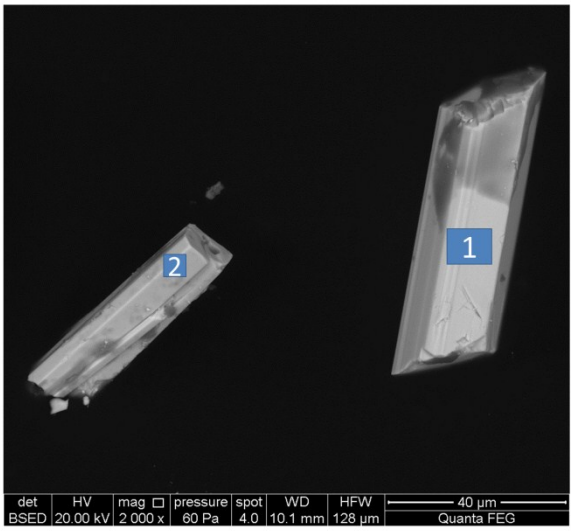


**Figure S2(e)**. EDS analysis for $Cs_2(UO_2)_3(GeO_4)_2$.

**Table S1(e)**. Atom ratio of $Cs_2(UO_2)_3(GeO_4)_2$. (U is keep as 3)

| | U | Ge | Cs |
|---|---|---|---|
| Point1 | 3 | 2.44 | 2.24 |
| Point2 | 3 | 2.87 | 2.29 |
| Average | 3 | 2.66 | 2.27 |

**Table S2.** Results of Bond valence calculation for $K_8BrF(UO_2)_3(Ge_2O_7)_2$, $Rb_6(UO_2)_3(Ge_2O_7)_2{\cdot}0.5H_2O$, $Cs_6(UO_2)_2Ge_8O_{21}$, and $\boldsymbol{A}^+_2(UO_2)_3(GeO_4)_2$ ($\boldsymbol{A}^+$ = $Rb^+$, $Cs^+$), respectively. Note that for an atom, the corresponding valence V is obtained through the following formula:

$$V = \sum_i exp[(R_i - d_i)/b]$$

Here the bond valence parameter $R_i$and constant $b$ of hexavalent U are taken from Burn.[2] The bond valence parameter $R_i$and constant $b$ of other elements are provided by Brese and O'Keeffe.[3, 4]

(a) BVS calculation for $K_8BrF(UO_2)_3(Ge_2O_7)_2$.

| | U(1) | U(2) | U(3) | Ge(1) | Ge(2) | K(1) | K(2) | K(3) | K(4) | Σ |
|---|---|---|---|---|---|---|---|---|---|---|
| **O(1)** | 2.2294$^{\times 2\downarrow}$ | | | | | 2.7261 | | 2.942 | | 2.039 |
| **O(2)** | | 2.2141$^{\times 2\downarrow}$ | | | 1.8070 | 2.6787 | 2.9075 | | | 2.089 |
| **O(3)** | | 1.8072$^{\times 2\downarrow}$ | | | | 2.6929 | 2.9909 | | | 2.011 |
| **O(4)** | | | | 1.7210 | 1.7376 | | 2.8103<br>3.3141 | | | 2.128 |
| **O(5)** | | | 2.2299$^{\times 2\downarrow}$ | 1.7051 | 1.6595 | | | 3.1104 | 3.0509 | 1.966 |
| **O(6)** | 2.2671$^{\times 2\downarrow}$ | | | | | | | 3.0127<br>3.0135 | 2.9647 | 1.930 |
| **O(7)** | 1.8389$^{\times 2\downarrow}$ | | | | | 2.7403 | | | 2.5753 | 1.986 |
| **O(8)** | | | 1.8171$^{\times 2\downarrow}$ | | 1.7109 | | 2.7401 | 2.8104 | 3.0206 | 2.001 |
| **O(9)** | | | 2.2608$^{\times 2\downarrow}$ | | | | 3.3881 | | 3.0170 | 2.044 |
| **O(10)** | | 2.21$^{\times 2\downarrow}$ | | 1.7337<br>1.7342 | | | 3.1614 | | 2.8043 | 1.980 |
| **Br(1)** | | | | | | 3.1254<br>3.2347 | 3.0746<br>3.4651 | 3.2255<br>3.4430 | | 1.039 |
| **F(1)** | | | | | | 2.5579<br>2.5669 | 2.9525 | 3.2909 | 2.8581 | 0.625 |
| **Σ** | 5.651 | 6.039 | 5.797 | 4.276 | 4.256 | 1.759 | 1.221 | 0.892 | 0.926 | |

(b) BVS calculation for $Rb_6(UO_2)_3(Ge_2O_7)_2 \cdot 0.5H_2O$.

| | **U(1)** | **U(2)** | **U(3)** | **Ge(1)** | **Ge(2)** | **Rb(1)** | **Rb(2)** | **Rb(3)** | **Rb(4)** | **Σ** |
|---|---|---|---|---|---|---|---|---|---|---|
| **O(1)** | 2.2331$^{\times 2\downarrow}$ | | | 1.7071 | | | 3.1296 | | 2.9922 | 2.038 |
| **O(2)** | | | | 1.7576 | 1.7579 | 2.9729<br>3.4736 | 3.3052 | | | 2.193 |
| **O(3)** | | | 2.2402$^{\times 2\downarrow}$ | 1.7242 | | | 3.0554 | 3.1178 | | 1.959 |
| **O(4)** | | 2.2334$^{\times 2\downarrow}$ | | | 1.7373 | 3.0381 | | | 2.941 | 1.998 |
| **O(5)** | | | 2.2471$^{\times 2\downarrow}$ | | 1.6742 | 3.2207 | | 3.0893 | | 2.070 |
| **O(6)** | | | 1.8058$^{\times 2\downarrow}$ | | | 2.9086 | 2.9473 | 3.0936 | | 2.033 |
| **O(7)** | | 2.1967$^{\times 2\downarrow}$ | | 1.7468 | | 3.2567 | | 2.8746 | | 1.999 |
| **O(8)** | 2.2502$^{\times 2\downarrow}$ | | | | 1.7297 | | 3.0570<br>3.1024 | | | 1.934 |
| **O(9)** | 1.7953$^{\times 2\downarrow}$ | | | | | | 3.6024 | 2.7782 | 2.7422 | 2.177 |
| **O(10)** | | 1.7967$^{\times 2\downarrow}$ | | | | 2.9515 | | 2.9945 | 2.7326 | 2.199 |
| **OW1** | | | | | | 3.1866 | 3.2841 | | | 0.313 |
| **Σ** | 5.953 | 6.091 | 5.875 | 4.161 | 4.274 | 0.864 | 0.741 | 0.891 | 0.854 | |

(c) BVS calculation for $Cs_6(UO_2)_2Ge_8O_{21}$.

| | U(1) | U(2) | Ge(1) | Ge(2) | Ge(3) | Ge(4) | Cs(1) | Cs(2) | Cs(3) | Cs(4) | Σ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **O(1)** | | | 2.0108 | | 2.2023 | 2.1940 | 3.4874 | 3.2398 | | | 1.248 |
| **O(2)** | | 2.2629$^{\times 2\downarrow}$ | | 1.7196 | | | 3.1425<br>3.1684 | | | 2.9257<br>3.2772 | 2.349 |
| **O(3)** | | | | 1.7590 | 1.7661 | | 3.3961 | 3.5577 | | 3.1337 | 2.184 |
| **O(4)** | | | | 1.7522 | | 1.7662 | 3.0610 | 3.3311 | | 3.4540 | 2.261 |
| **O(5)** | 1.8243$^{\times 2\downarrow}$ | | | | | | | 3.2311 | 3.1485<br>3.6696 | | 1.821 |
| **O(6)** | | | 1.8134 | 1.7370 | | | | 3.4495 | 3.0971 | | 2.089 |
| **O(7)** | 2.2169$^{\times 2\downarrow}$ | | | | 1.6916 | | | 3.1818 | 3.2929 | | 2.093 |
| **O(8)** | | | 1.7596 | | 1.7668 | | | 3.0804 | 3.6288 | | 2.124 |
| **O(9)** | 2.2278$^{\times 2\downarrow}$ | | | | | 1.7159 | | 3.3469 | 3.1665<br>3.5602 | | 2.041 |
| **O(10)** | | 1.8239$^{\times 2\downarrow}$ | | | | | 3.1333 | 3.1287 | | 3.1377<br>3.6933 | 2.004 |
| **O(11)** | | 2.2327$^{\times 2\downarrow}$ | 1.7365 | | | | 3.2407<br>3.4139 | | | 3.1746 | 2.022 |
| **O(12)** | | | 1.7493 | | | 1.7122 | | 3.0627 | 3.7105 | | 2.303 |
| **O(13)** | | | | | 1.7944 | 1.7944 | | 3.4031 | 3.1174 | | 1.985 |
| **Σ** | 5.876 | 5.742 | 3.8352 | 4.0694 | 3.949 | 4.026 | 0.894 | 1.175 | 0.821 | 0.859 | |

(d) BVS calculation for $Rb_2(UO_2)_3(GeO_4)_2$.

| | **U(1)** | **U(2)** | **U(3)** | **Ge(1)** | **Rb(1)** | **Σ** |
|---|---|---|---|---|---|---|
| **O(1)** | | | 1.7918 | | 2.7862 | 2.126 |
| **O(2)** | 2.4659 | | 2.5942 | 2.0275 | | 1.708 |
| **O(3)** | 2.4045$^{\times 2\downarrow}$ | 2.3348$^{\times 2\downarrow}$ | | 1.7629 | 3.0859 | 2.244 |
| **O(4)** | | | 1.7973 | | 2.8864 | 1.993 |
| **O(5)** | 1.8149 | | | | 2.8946 | 1.929 |
| **O(6)** | | | 2.3159<br>2.3160<br>2.3212$^{\times 2\downarrow}$ | 1.7612 | 3.4165 | 2.167 |
| **O(7)** | | 1.8107 | | | 3.0977<br>3.5654 | 1.848 |
| **O(8)** | | 2.3508 | | 1.9024 | | 1.861 |
| **O(9)** | 2.2762$^{\times 2\downarrow}$ | 2.3650$^{\times 2\downarrow}$ | | 1.7699 | | 2.100 |
| **O(10)** | 1.8040 | | | | 2.9415 | 1.920 |
| **O(11)** | | 1.7993 | | | 2.9673 | 1.914 |
| **Σ** | 5.836 | 5.916 | 5.913 | 3.997 | 1.206 | |

(e) BVS calculation for $Cs_2(UO_2)_3(GeO_4)_2$.

| | **U(1)** | **U(2)** | **U(3)** | **Ge(1)** | **Cs(1)** | **∑** |
|---|---|---|---|---|---|---|
| **O(1)** | | | 1.7970 | | 2.9001 | 2.165 |
| **O(2)** | 2.4735 | | 2.5665 | 2.0410 | | 1.687 |
| **O(3)** | 2.4001$^{\times 2\downarrow}$ | 2.3349<br>2.3350 | | 1.7679 | 3.2875 | 2.096 |
| **O(4)** | | | 1.8049 | | 2.9929 | 2.020 |
| **O(5)** | 1.8130 | | | | 3.0611 | 1.983 |
| **O(6)** | | | 2.3169$^{\times 2\downarrow}$<br>2.3294$^{\times 2\downarrow}$ | 1.7600 | 3.6579 | 2.139 |
| **O(7)** | | 1.8122 | | | 3.2845<br>3.3933 | 1.909 |
| **O(8)** | | 2.3655 | | 1.8941 | | 1.875 |
| **O(9)** | 2.2835$^{\times 2\downarrow}$ | 2.3812$^{\times 2\downarrow}$ | | 1.7716 | | 2.070 |
| **O(10)** | 1.7996 | | | | 3.0313 | 1.995 |
| **O(11)** | | 1.7928 | | | 3.0646 | 1.984 |
| **∑** | 5.840 | 5.883 | 5.847 | 3.981 | 1.318 | |

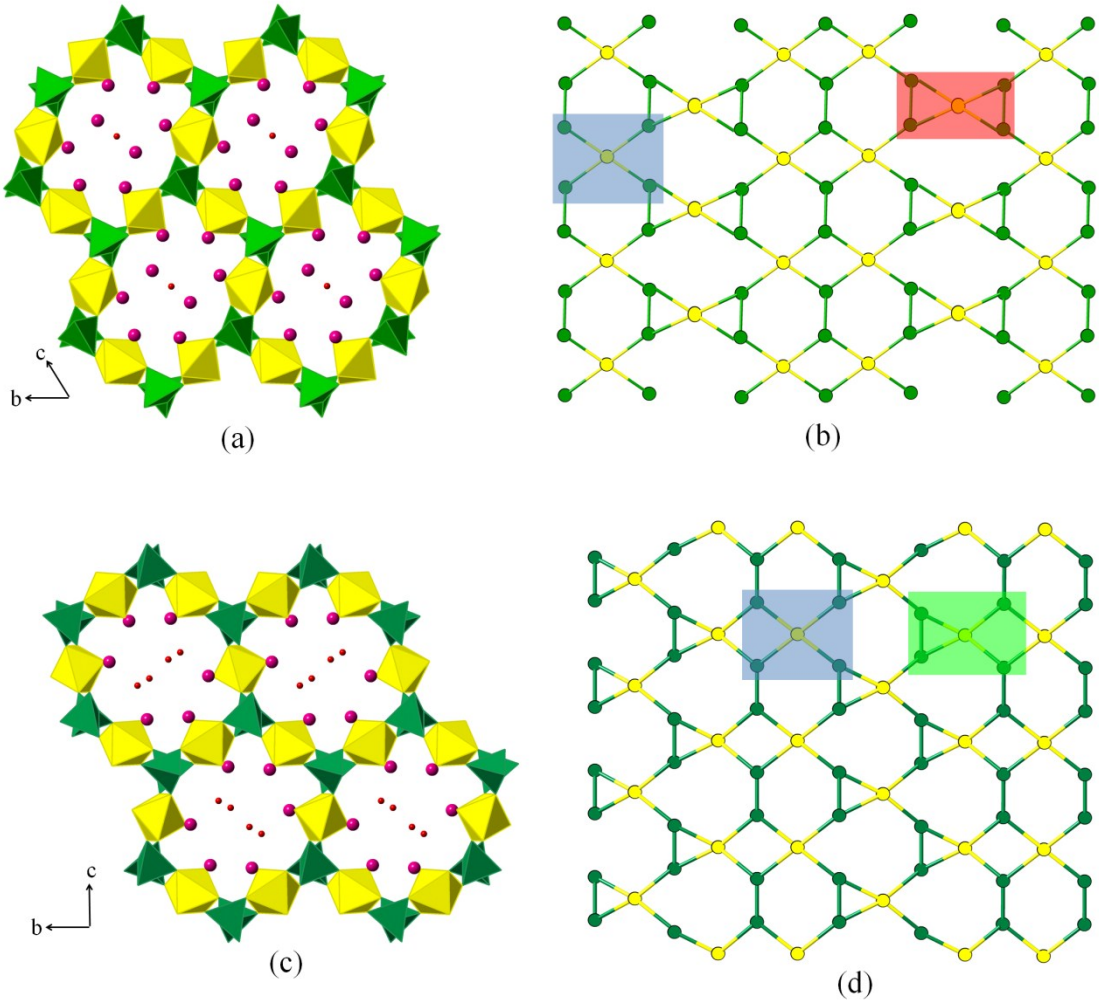


**Figure S3.** (a) Structure of $Rb_6(UO_2)_3(Ge_2O_7)_2{\cdot}0.5H_2O$ projected along ***a*** axis. (b) The unfolding wall of 12-membered channels constructed by [$UGe_4$] pentamers (**A** type) and (**A2** type) in the structure of $Rb_6(UO_2)_3(Ge_2O_7)_2{\cdot}0.5H_2O$. (c) Structure of $Cs_6(UO_2)_3(Ge_2O_7)_2{\cdot}4H_2O$[5] projected along ***a*** axis. (d) The unfolding wall of 12-membered channels consisting of [$UGe_4$] pentamers (**A** type) and (**A1** type) in the structure of $Cs_6(UO_2)_3(Ge_2O_7)_2{\cdot}4H_2O$.

**Table S3** U=O bond lengths in uranyl $(UO_2)^{2+}$ ions for $A^+_2(UO_2)_3(GeO_4)_2$ ($A^+$ = Rb, Cs) compounds and corresponding to the stretching frequencies of $\nu_1$ and $\nu_3$ vibrational modes.

| Compounds | U=O bonds | Bond lengths (Å) | Calculated ($cm^{-1}$) | | | | Experimental ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | | $\nu_1$ | $\nu_3$ | Average of $\nu_1$ | Average of $\nu_3$ | $\nu_1$ | $\nu_3$ |
| $Cs_2(UO_2)_3(GeO_4)_2$ | U(1)=O(10) | 1.798(5) | 812 | 881 | 809 | 878 | 721, 753, 781, **813**, | 830, 836, 851,**870**, 909, |
| | U(1)=O(5) | 1.815(5) | 796 | 860 | | | | |
| | U(2)=O(11) | 1.792(5) | 818 | 890 | | | | |
| | U(2)=O(7) | 1.810(5) | 800 | 865 | | | | |
| | U(3)=O(1) | 1.793(5) | 818 | 889 | | | | |
| | U(3)=O(4) | 1.799(5) | 811 | 880 | | | | |
| $Rb_2(UO_2)_3(GeO_4)_2$ | U(1)=O(10) | 1.804(5) | 806 | 873 | 807 | 874 | 729, 757, 783, **818,** | 837, 854, **867,** 908, |
| | U(1)=O(5) | 1.816(5) | 795 | 858 | | | | |
| | U(2)=O(11) | 1.802(5) | 808 | 876 | | | | |
| | U(2)=O(7) | 1.812(5) | 799 | 863 | | | | |
| | U(3)=O(1) | 1.789(6) | 821 | 893 | | | | |
| | U(3)=O(4) | 1.798(6) | 812 | 881 | | | | |

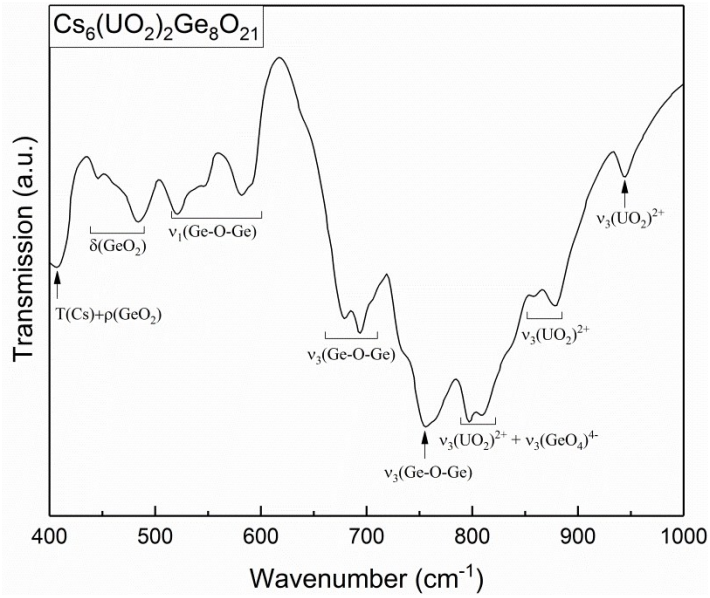


**Figure S4.** Infrared spectra of $Cs_6(UO_2)_2Ge_8O_{21}$ in the 400 − 1000 $cm^{-1}$ region.

**References**

(1) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, Taylor, M. Taylor and J. v. D. Streek, *J. Appl. Crystallogr.,* 2006, **39**, 453-457.

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