Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

# Supporting Information for

# An effective method for the synthesis of 3D inorganic Ln(III)/K(I) sulfate open frameworks with unusually high thermal stability: *In situ* generation of sulfate anions

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### *Electronic Structure Calculations*

Single-crystal structural data of **3** and **7** were used for theoretical calculations. The ab initio band structure calculations and density of states (DOS) were performed using the computer code CASTEP.[1] The code employs density functional theory (DFT) using a plane-wave basis set with Vanderbilt norm-conserving pseudo potentials to approximate the interactions between core and valence electrons.[2] The exchange-correlation energy was calculated using the Perdew-Burke-Ernzerhof modification to the generalized gradient approximation. The number of plane waves included in the basis is determined by a kinetic-energy cutoff of 360 eV for $KGd(SO_4)_2H_2O$ or 340 eV for $KEr(SO_4)_2H_2O$. The numerical integration of the Brillouin zone is performed using a 2 × 2 × 2 Monkhorst-Pack k-point sampling for both A and B. Pseudo atomic calculations were performed for H-$1s^1$, O-$2s^22p^4$, S-$3s^23p^4$, K-$3s^23p^64s^1$, Gd-$4f^75s^25p^65d^16s^2$, and Er-$4f^{12}5s^25p^66s^2$. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code.

### Optical Properties and Electronic Structures.

The optical band gaps were measured by the diffuse-reflectance spectra at room temperature. The band gaps are measured to be 4.7 and 4.2 eV for **3** and **7**, respectively (Fig. S2†). Such values suggest the insulator behavior.

To further understand the chemical bonding in **3** and **7**, the band structures and DOS calculations based on the DFT method were performed. The calculated band structures of **3** and **7** along high symmetry points of the first Brillouin zone are plotted in Fig. S3†. As shown in Fig. S3a†, the top of the valence bands (VBs) is almost flat, whereas the bottom of the conduction bands (CBs) displays a small dispersion for **3**. The lowest energy (5.35745 eV) of CBs is located at the G point and the highest energy (–0.00237 eV) of VBs is located at the Z point. Hence, $KGd(SO_4)_2H_2O$ has an indirect band gap of around 5.36 eV. Both the top of VBs and the bottom of the CBs are almost flat for **7**. The lowest energy (3.33187 eV) of CBs is located at the G point, and the highest energy (–0.00015 eV) of VBs is also located at the G point. Accordingly, compound **3** displays a direct band gap of around 3.33 eV (Fig. S3b†). The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of **3** and **7** are listed in Table S3†. The calculated band gap of either **3** or **7** is somehow different from the experimental value. This is not surprising as it is well known that the generalized gradient approximation does not accurately describe the eigenvalues of the electronic states, which causes quantitative underestimation of the band gaps, especially for insulators.[3] The bands can be assigned according to the total and partial DOS, as plotted in Fig. S4†. For **3**, the CBs above the Fermi level are mainly derived from Gd-5d, K-3p, O-3p and S-3p states. The VBs from –4.96 eV to the Fermi level is mainly derived from O-2p state, and those from –12.04 to 4.96 eV are mainly composed of Gd-4f, K-3p, O-2p, S-3s, and S-3p states. The lowest VBs in the range from –28.44 to –16.43 eV mostly arise from Gd-5p, K-3s, K-4s, S-3s, S-3p, and O-2p states. For **7**, the bands above the Fermi level are mainly derived from Er-4f, K-3p, and S-3p states. The VBs from –5.01 eV to the Fermi level are mainly composed of Er-4f and O-2p states, whereas the Er-4f, K-3p, S-3p, and O-2p states dominate the VBs ranging from –12.15 to –5.01 eV. In addition, the VBs ranging from –24.73 to –17.50 eV are mainly composed of Er-5p, S-3p, S-3s, and O-2s states.

1. M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne. *J. Phys*.: *Condens*. *Matter*., 2002, **14,** 2717–2744;

2. J. S. Lin, A. Qteish, M. C. Payne, and V. Heine *Phy. Rev. B.*, 1993, **47,** 4174–4180.

3. T. Bataille and D. Louër, J. Mater. Chem., 2002, 12, 3487–3493..

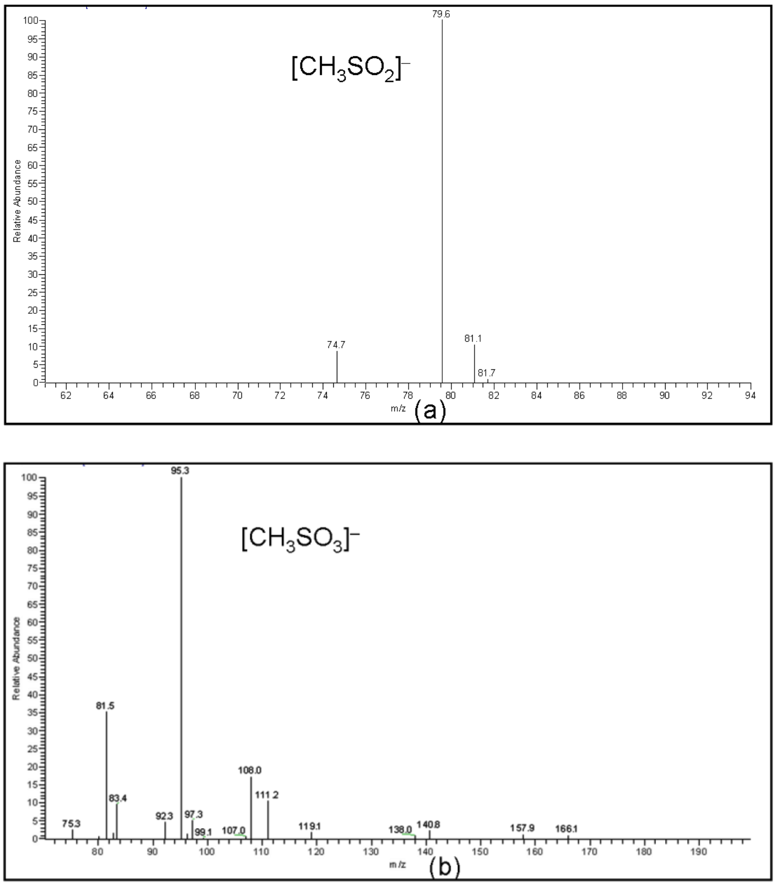


**Fig. S1** ESI-MS spectra of the reaction mixture (a) after 72 h and (b) after 96 h.

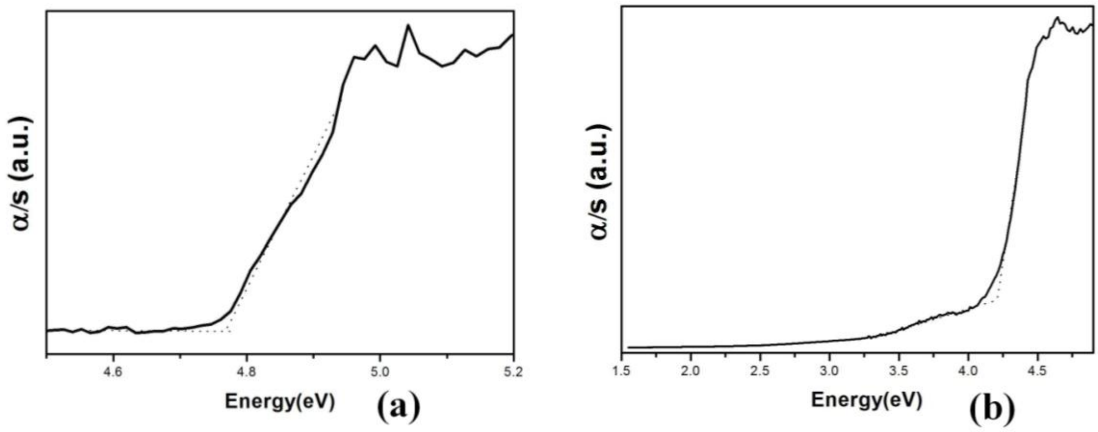


**Fig. S2** Optical diffuse reflectance spectra for **3** (a) and **7** (b).

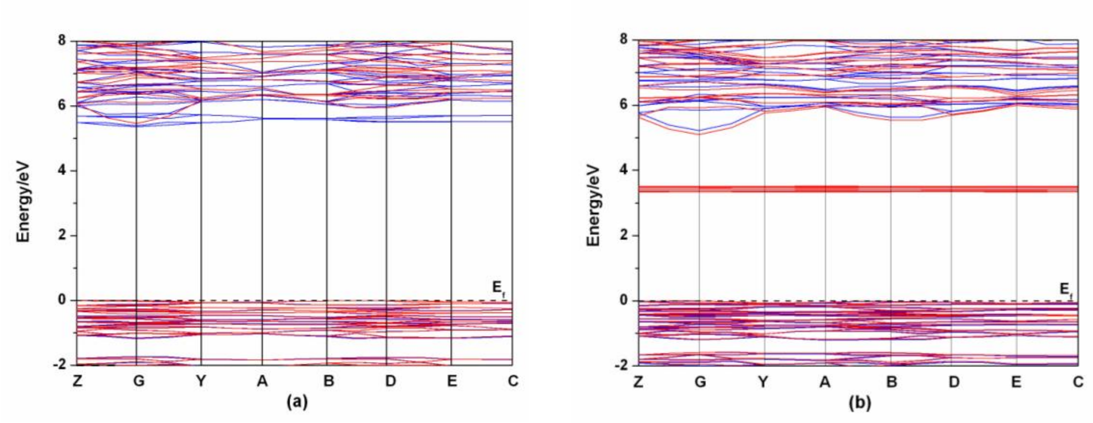


**Fig. S3** Band structures for **3** (a) and **7** (b). The Fermi level is set at 0 eV.

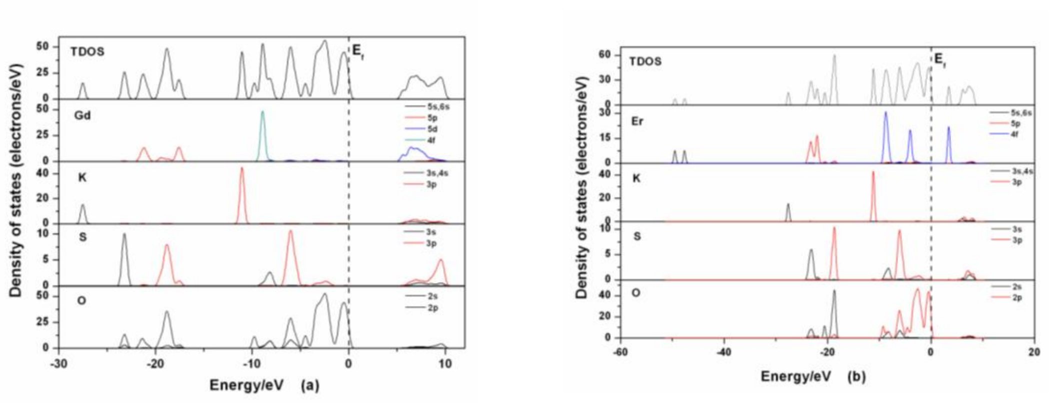
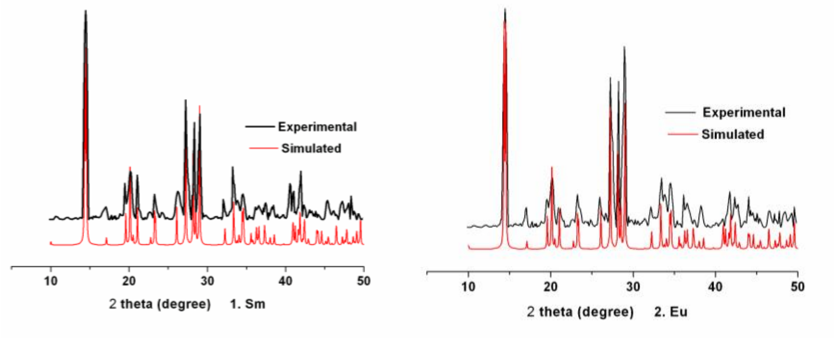


**Fig. S4** Total and partial density of states of **3** (a) and **7** (b). The Fermi level is set at 0 eV.



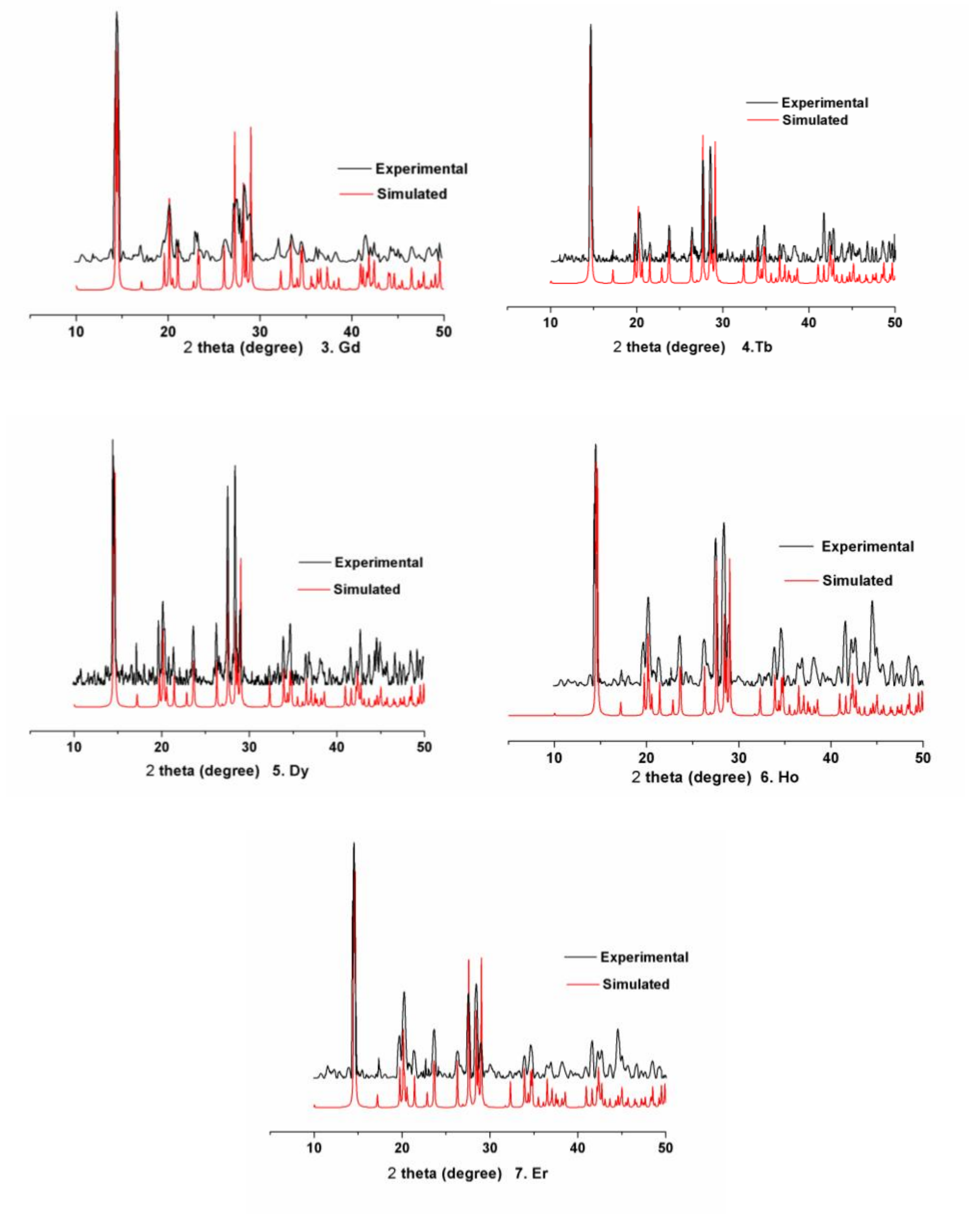
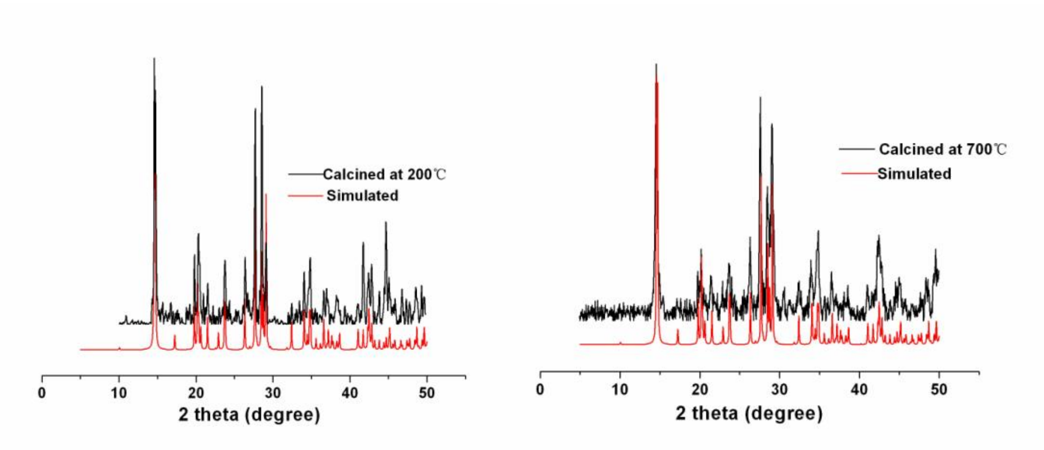


**Fig. S5** Simulated and experimental PXRD patterns of **1–7** at 30 °C.



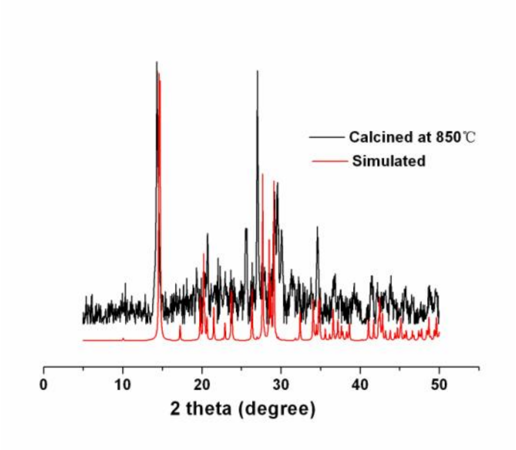


**Fig. S6** XRD patterns of compound **6** after calcination at different temperatures.

**Table S1** Crystallographic data for **1–7.**

| Compounds | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| Formula | $KSm(SO_4)_2H_2O$ | $KEu(SO_4)_2H_2O$ | $KGd(SO_4)_2H_2O$ | $KTb(SO_4)_2H_2O$ | $KDy(SO_4)_2H_2O$ | $KHo(SO_4)_2H_2O$ | $KEr(SO_4)_2H_2O$ |
| M (g mol$^{-1}$) | 399.59 | 401.20 | 406.49 | 408.16 | 411.74 | 414.17 | 416.52 |
| Cryst syst | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/C$ | $P2_1/C$ | $P2_1/C$ | $P2_1/C$ | $P2_1/C$ | $P2_1/C$ | $P2_1/C$ |
| $a$ (Å) | 10.069(3) | 10.084(1) | 10.129(5) | 10.128(3) | 10.107(4) | 10.079(4) | 10.068(2) |
| $b$ (Å) | 8.466(8) | 8.429(8) | 8.391(3) | 8.326(8) | 8.290(3) | 8.257(3) | 8.234(4) |
| $c$ (Å) | 10.377(3) | 10.363(1) | 10.357(7) | 10.344(5) | 10.306(5) | 10.280(5) | 10.266(3) |
| $\beta$ (°) | 118.938(7) | 119.023(1) | 119.152(6) | 119.305(1) | 119.318(3) | 119.285(5) | 119.382(1) |
| $V$ (Å$^3$) | 774.2(2) | 770.2(1) | 768.8(7) | 760.8(5) | 752.9(5) | 746.2(5) | 741.6(5) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_c$ (g cm$^{-3}$) | 3.428 | 3.46 | 3.51 | 3.56 | 3.63 | 3.69 | 3.73 |
| $\mu$ (mm$^{-1}$) | 8.68 | 9.25 | 9.73 | 10.42 | 11.06 | 11.74 | 12.46 |
| $F$(000) | 748 | 752 | 756 | 760 | 764 | 768 | 772 |
| GOF | 1.08 | 1.02 | 1.13 | 1.12 | 1.26 | 0.80 | 1.25 |
| $R_1$[a] | 0.0219 | 0.0375 | 0.0225 | 0.0189 | 0.0188 | 0.0243 | 0.0341 |
| $R_1$[b] | 0.0210 | 0.0410 | 0.0237 | 0.0197 | 0.0195 | 0.0289 | 0.0343 |
| $wR_2$[a] | 0.0542 | 0.0858 | 0.0569 | 0.0470 | 0.0480 | 0.0904 | 0.896 |
| $wR_2$[b] | 0.0548 | 0.0871 | 0.0577 | 0.0474 | 0.0482 | 0.1338 | 0.896 |

[a] $R = \sum (||F_o| - |F_c||)/\sum |F_o|$, $wR = \{ \sum w[(F_o^2 - F_c^2)^2]/ \sum w[(F_o^2)^2]\}^{1/2}$; $[F_o > 4\sigma (F_o)]$.

[b] Based on all data.

**Table S2** Selected bond lengths and angles for **1–7.**

| Compounds | **Sm-1** | **Eu-2** | **Gd-3** | **Tb-4** | **Dy-5** | **Ho-6** | **Er-7** |
|---|---|---|---|---|---|---|---|
| Ln 1—O2 | 2.442(4) | 2.432(5) | 2.355 (4) | 2.338 (4) | 2.329 (3) | 2.526 (6) | 2.373 (6) |
| Ln 1—O3$^{iii}$ | 2.397(3) | 2.378(4) | 2.353 (3) | 2.332 (3) | 2.391 (3) | 2.323 (5) | 2.369 (7) |
| Ln 1—O4$^{i}$ | 2.357 (3) | 2.370(5) | 2.347 (3) | 2.330 (3) | 2.552 (4) | 2.389 (5) | 2.534 (8) |
| Ln 1—O5 | 2.435 (3) | 2.417 (5) | 2.366 (3) | 2.346 (3) | 2.319 (4) | 2.303 (6) | 3.5591(2) |
| Ln 1—O6 | 2.667 (3) | 2.635 (5) | 2.418 (3) | 2.412 (3) | 2.679 (4) | 2.292 (6) | 2.294 (7) |
| Ln 1—O7$^{ii}$ | 2.386 (3) | 2.387 (6) | 2.423 (3) | 2.565 (3) | 2.314 (3) | 2.311 (5) | 2.288 (6) |
| Ln 1—O8$^{iv}$ | 2.435 (3) | 2.346 (4) | 2.597 (4) | 2.403 (3) | 2.318 (3) | 2.662 (6) | 2.298 (7) |
| Ln 1—O9W | 2.524 (3) | 2.484 (5) | 2.468 (4) | 2.435 (3) | 2.419 (3) | 2.392 (5) | 2.386 (7) |
| K1—O1 | 2.777 (4) | 2.820 (5) | 2.686 (4) | 2.682 (4) | 2.828 (4) | 2.808 (6) | 2.897(2) |
| K1—O2$^{i}$ | 2.877 (4) | 2.876 (6) | 3.037 (5) | 3.054(4) | 2.928 (4) | 2.915 (6) | 2.903(2) |
| K1—O3$^{iii}$ | 3.177 (3) | 2.955 (6) | 3.258 (4) | 3.279(3) | 2.905 (4) | 2.891 (6) | 2.816(2) |
| K1—O4$^{iii}$ | 3.117 (3) | 2.973 (5) | 3.081 (4) | 3.074 (3) | 2.911 (4) | 2.913 (6) | 2.890(2) |
| K1—O5$^{v}$ | 2.825 (3) | 2.718 (6) | 2.955 (4) | 2.937 (3) | 3.060 (4) | 3.284 (6) | 2.675(2) |
| K1—O6$^{vii}$ | 2.879 (3) | 2.955 (6) | 2.894 (4) | 2.828 (3) | 2.679 (4) | 3.057 (6) | 3.053(2) |
| K1—O7$^{vi}$ | 2.994 (3) | 3.094 (5) | 2.831 (4) | 2.910 (3) | 3.284 (4) | 3.067 (6) | 3.285(2) |
| K1—O8$^{vi}$ | 2.868 (3) | 3.214 (6) | 2.905 (4) | 2.904 (3) | 3.068 (4) | 2.662 (6) | 3.054(2) |
| K1—O9W$^{viii}$ | 3.002 (4) | 3.017 (5) | 3.015 (4) | 3.013 (3) | 3.004 (4) | 3.001 (6) | 3.009(2) |
| O1—S1—O4 | 113.0 (2) | 111.9 (3) | 107.5 (2) | 111.0 (2) | 111.8 (2) | 112.4 (3) | 112.3 (4) |
| O1—S1—O2 | 106.3 (3) | 107.5 (3) | 111.4 (2) | 111.2 (2) | 107.7 (2) | 107.3 (3) | 107.2 (4) |
| O4—S1—O2 | 110.7 (2) | 111.1 (3) | 111.8 (2) | 110.1 (2) | 111.4 (2) | 112.0 (3) | 111.3 (4) |
| O1—S1—O3 | 111.1 (2) | 109.7 (3) | 110.9 (2) | 109.8 (2) | 110.4 (2) | 110.2 (3) | 110.7 (4) |

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+2, −*y*, −*z*+1; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*, −*y*+1/2, *z*+1/2; (v) −*x*+2, *y*−1/2, −*z*+3/2; (vi) *x*, −*y*−1/2, *z*+1/2; (vii) *x*, −*y*+1/2, *z*−1/2; (viii) −*x*+2, *y*+1/2, −*z*+3/2; (ix) *x*, −*y*−1/2, *z*−1/2; (x) −*x*+1, *y*−1/2, −*z*+1/2.

**Table S3** State Energies (eV) of the L-CB and H-VB of **3** and **7**.

| $KGd(SO_4)_2.H_2O$ | | |
|---|---|---|
| K point | L-CB | H-VB |
| Z ( 0.000,0.000,0.500) | 5.48733 | -0.00237 |
| G ( 0.000,0.000,0.000) | 5.35745 | -0.0059 |
| Y ( 0.000,0.500,0.000) | 5.47689 | -0.06914 |
| A ( -0.500,0.500,0.000) | 5.59182 | -0.06274 |
| B ( -0.500,0.000,0.000) | 5.58467 | -0.01506 |
| D ( -0.500,0.000,0.500) | 5.50538 | -0.01204 |
| E ( -0.500,0.500,0.500) | 5.50869 | -0.04691 |
| C ( 0.000,0.500,0.500) | 5.51322 | -0.05785 |
| $KEr(SO_4)_2.H_2O$ | | |
| K point | L-CB | H-VB |
| Z ( 0.000,0.000,0.500) | 3.33385 | -0.01767 |
| G ( 0.000,0.000,0.000) | 3.33187 | -0.00015 |
| Y ( 0.000,0.500,0.000) | 3.33378 | -0.07707 |
| A ( -0.500,0.500,0.000) | 3.33522 | -0.05194 |
| B ( -0.500,0.000,0.000) | 3.33815 | -0.01834 |
| D ( -0.500,0.000,0.500) | 3.33828 | -0.03304 |
| E ( -0.500,0.500,0.500) | 3.33684 | -0.0807 |
| C ( 0.000,0.500,0.500) | 3.33209 | -0.06033 |

**Table S4a** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $SmK(SO_4)_2 \cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Sm1 | 4e | 1 | 0.7613(5) | 0.1552(8) | 0.0323(6) | 0.0112(2) |
| K1 | 4e | 1 | 1.2859(2) | 0.1848(6) | 0.3076(8) | 0.0248 (2) |
| S1 | 4e | 1 | 0.9863(2) | 0.1868(3) | −0.1099(6) | 0.0152 (2) |
| S2 | 4e | 1 | 0.5497(9) | 0.1322(1) | 0.1775(6) | 0.0117 (2) |
| O1 | 4e | 1 | 1.0371 (5) | 0.2510 (4) | 0.0357 (4) | 0.0467 (1) |
| O2 | 4e | 1 | 0.8419 (4) | 0.1046 (5) | −0.1511 (4) | 0.0344 (9) |
| O3 | 4e | 1 | 0.9585 (4) | 0.3140 (4) | −0.2179 (4) | 0.0205 (7) |
| O4 | 4e | 1 | 1.0961 (3) | 0.0792 (4) | −0.1167 (4) | 0.0220 (7) |
| O5 | 4e | 1 | 0.5543 (3) | 0.2463 (4) | 0.0716 (3) | 0.0205 (7) |
| O6 | 4e | 1 | 0.6737 (3) | 0.0192 (4) | 0.2108 (4) | 0.0213 (7) |
| O7 | 4e | 1 | 0.4015 (3) | 0.0536 (4) | 0.1127 (4) | 0.0222 (7) |
| O8 | 4e | 1 | 0.5716 (3) | 0.2123 (4) | 0.3114 (3) | 0.0182 (6) |
| $O9_W$ | 4e | 1 | 0.8115 (4) | 0.4481 (4) | 0.0393 (4) | 0.0281 (8) |
| H1A | 4e | 1 | 0.8687 | 0.4836 | 0.0068 | 0.034 |
| H1B | 4e | 1 | 0.7712 | 0.5112 | 0.0742 | 0.034 |

[a] Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

**Table S4b** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $EuK(SO_4)_2\cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Eu1 | 4e | 1 | 0.7404 (4) | 0.1515(4) | 0.4658 (7) | 0.0121 (5) |
| K1 | 4e | 1 | 0.7874 (2) | −0.1813(1) | 0.8096 (3) | 0.0258 (4) |
| S1 | 4e | 1 | 0.9496(1) | 0.1332(5) | 0.3209 (4) | 0.0121 (3) |
| S2 | 4e | 1 | 0.4921 (1) | −0.1914(4) | 0.3934 (9) | 0.0165 (4) |
| O1 | 4e | 1 | 1.0985 (5) | 0.0572 (5) | 0.3869 (5) | 0.0219 (1) |
| O2 | 4e | 1 | 0.9261 (5) | 0.2133 (5) | 0.1852 (5) | 0.0202 (1) |
| O3 | 4e | 1 | 0.9448 (5) | 0.2492 (5) | 0.4263 (5) | 0.0216 (1) |
| O4 | 4e | 1 | 0.8276 (5) | 0.0181 (5) | 0.2894 (5) | 0.0223 (1) |
| O5 | 4e | 1 | 0.5575 (8) | −0.2603(7) | 0.5386 (6) | 0.064 (2) |
| O6 | 4e | 1 | 0.3514 (6) | −0.1090(6) | 0.3636 (7) | 0.0398 (15) |
| O7 | 4e | 1 | 0.5970 (5) | −0.0818(5) | 0.3802 (5) | 0.0216 (10) |
| O8 | 4e | 1 | 0.4555 (5) | −0.3156(5) | 0.2809 (5) | 0.0186 (10) |
| O9$_W$ | 4e | 1 | 0.6819 (6) | 0.4391 (5) | 0.4544 (5) | 0.0284 (12) |
| H1A | 4e | 1 | 0.6689 | 0.4818 | 0.5218 | 0.034* |
| H1B | 4e | 1 | 0.6749 | 0.4948 | 0.3830 | 0.034* |

[a] Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

**Table S4c** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $GdK(SO_4)_2\cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Gd1 | 4e | 1 | 0.2576(0) | 0.1480(4) | 0.0360(5) | 0.0091(9) |
| K1 | 4e | 1 | −0.2111(5) | 0.3232(6 ) | −0.1884(9) | 0.0237 (3) |
| S1 | 4e | 1 | 0.5018(6) | −0.1966(7) | 0.1027(4) | 0.0132 (3) |
| S2 | 4e | 1 | 0.0506(6) | 0.1342(3) | 0.1803(4) | 0.0104 (3) |
| O1 | 4e | 1 | 0.4229 (6) | −0.2711 (5) | −0.0412 (4) | 0.0496 (1) |
| O2 | 4e | 1 | 0.6385 (5) | −0.1143 (5) | 0.1220 (5) | 0.0339 (1) |
| O3 | 4e | 1 | 0.5469 (4) | −0.3190 (4) | 0.2192 (4) | 0.0173 (7) |
| O4 | 4e | 1 | 0.4028 (4) | −0.0850 (4) | 0.1236 (4) | 0.0175 (8) |
| O5 | 4e | 1 | −0.0992 (4) | 0.0602 (5) | 0.1131 (4) | 0.0193 (8) |
| O6 | 4e | 1 | 0.0759 (4) | 0.2118 (4) | 0.3171 (4) | 0.0168 (7) |
| O7 | 4e | 1 | 0.0576 (4) | 0.2522 (4) | 0.0764 (4) | 0.0189 (8) |
| O8 | 4e | 1 | 0.1700 (4) | 0.0167 (4) | 0.2087 (4) | 0.0206 (8) |
| O9$_W$ | 4e | 1 | 0.3228 (4) | 0.4332 (4) | 0.0500 (4) | 0.0228 (8) |
| H1A | 4e | 1 | 0.2490 | 0.5070 | 0.0121 | 0.027 |
| H1B | 4e | 1 | 0.4203 | 0.4635 | 0.0930 | 0.027 |

[a] Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

**Table S4d** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $TbK(SO_4)_2\cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Tb1 | 4e | 1 | 0.7563(1) | 0.1454(6) | 0.5370(1) | 0.0094(5) |
| K1 | 4e | 1 | 0.2898(5) | 0.3270(4) | 0.3130(3) | 0.0238 (3) |
| S1 | 4e | 1 | 0.9987(8) | −0.1994(6) | 0.6006(8) | 0.0122 (2) |
| S2 | 4e | 1 | 0.5512(3) | 0.1358(7) | 0.6811(7) | 0.0106 (2) |
| O1 | 4e | 1 | 0.9148 (4) | −0.2770 (4) | 0.4574 (4) | 0.0347 (9) |
| O2 | 4e | 1 | 1.1340 (4) | −0.1161 (4) | 0.6147 (4) | 0.0261 (8) |
| O3 | 4e | 1 | 1.0489 (3) | −0.3205 (4) | 0.7199 (4) | 0.0173 (7) |
| O4 | 4e | 1 | 0.9028 (3) | −0.0861 (4) | 0.6255 (3) | 0.0170 (7) |
| O5 | 4e | 1 | 0.3999 (3) | 0.0624 (4) | 0.6130 (4) | 0.0193 (7) |
| O6 | 4e | 1 | 0.5591 (3) | 0.2545 (4) | 0.5779 (3) | 0.0187 (7) |
| O7 | 4e | 1 | 0.6688 (3) | 0.0160 (4) | 0.7073 (4) | 0.0202 (7) |
| O8 | 4e | 1 | 0.5772 (3) | 0.2134 (4) | 0.8182 (3) | 0.0169 (7) |
| $O9_W$ | 4e | 1 | 0.8256 (4) | 0.4277 (4) | 0.5522 (4) | 0.0219 (7) |
| H1A | 4e | 1 | 0.7571 | 0.4993 | 0.5166 | 0.026 |
| H1B | 4e | 1 | 0.9184 | 0.4545 | 0.5930 | 0.026 |

[a] Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

**Table S4e** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $DyK(SO_4)_2 \cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Dy1 | 4e | 1 | 0.7443(4) | 0.1440(1) | 0.4624 (2) | 0.0058 (2) |
| K1 | 4e | 1 | 0.7900(5) | −0.1706(1) | 0.8135 (6) | 0.0203 (3) |
| S1 | 4e | 1 | 0.9484(9) | 0.1359(5) | 0.3186 (6) | 0.0074 (2) |
| S2 | 4e | 1 | 0.4972(3) | 0.2014(0) | 0.5995 (5) | 0.0077 (2) |
| O1 | 4e | 1 | 0.9397 (4) | 0.2561 (4) | 0.4210 (4) | 0.0157 (7) |
| O2 | 4e | 1 | 1.1004 (4) | 0.0631 (4) | 0.3877 (4) | 0.0150 (7) |
| O3 | 4e | 1 | 0.9219 (4) | 0.2137 (4) | 0.1807 (3) | 0.0139 (7) |
| O4 | 4e | 1 | 0.8315 (4) | 0.0151 (4) | 0.2921 (4) | 0.0161 (7) |
| O5 | 4e | 1 | 0.6312 (4) | 0.1170 (4) | 0.6101 (4) | 0.0197 (8) |
| O6 | 4e | 1 | 0.4112 (4) | 0.2800 (4) | 0.4569 (4) | 0.0228 (8) |
| O7 | 4e | 1 | 0.5504 (4) | 0.3211 (4) | 0.7205 (4) | 0.0139 (7) |
| O8 | 4e | 1 | 0.4031 (4) | 0.0863 (4) | 0.6271 (4) | 0.0133 (7) |
| $O9_W$ | 4e | 1 | 0.6723 (4) | 0.4247 (4) | 0.4461 (4) | 0.0159 (7) |
| H1A | 4e | 1 | 0.6535 | 0.4679 | 0.5156 | 0.019* |
| H1B | 4e | 1 | 0.6642 | 0.4860 | 0.3704 | 0.019* |

[a] Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

**Table S4f** Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $HoK(SO_4)_2 \cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Ho1 | 4e | 1 | 0.2448(0) | −0.1433(4) | 0.46233 (3) | 0.0083 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| K1 | 4e | 1 | 0.2905 (2) | 0.3307 (2) | 0.3137 (2) | 0.0225 (4) |
| S1 | 4e | 1 | 0.4484 (2) | −0.1360(9) | 0.3190 (2) | 0.0100 (4) |
| S2 | 4e | 1 | −0.0030(6) | −0.2980 (2) | 0.0990 (2) | 0.0099 (4) |
| O1 | 4e | 1 | 0.4399 (6) | −0.2560 (7) | 0.4234 (6) | 0.0156 (1) |
| O2 | 4e | 1 | 0.3326 (6) | −0.0160 (7) | 0.2940 (6) | 0.0192 (1) |
| O3 | 4e | 1 | 0.6017 (6) | −0.0643 (7) | 0.3866 (6) | 0.0172 (1) |
| O4 | 4e | 1 | 0.4211 (6) | −0.2155 (7) | 0.1826 (6) | 0.0154 (1) |
| O5 | 4e | 1 | 0.0511 (7) | −0.1783 (7) | 0.2212 (6) | 0.0176 (1) |
| O6 | 4e | 1 | 0.1302 (7) | −0.3836 (7) | 0.1065 (7) | 0.0184 (1) |
| O7 | 4e | 1 | −0.0985 (6) | −0.4116 (7) | 0.1229 (6) | 0.0161 (1) |
| O8 | 4e | 1 | −0.0929 (7) | −0.2191 (7) | −0.0444 (6) | 0.0199 (1) |
| $O9_W$ | 4e | 1 | 0.1736 (7) | −0.4220 (7) | 0.4467 (8) | 0.0238 (1) |
| H1A | 4e | 1 | 0.1249 | −0.4674 | 0.3620 | 0.029 |
| H1B | 4e | 1 | 0.1963 | −0.4754 | 0.5256 | 0.029 |

[a]Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor

**Table S4g**Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $ErK(SO_4)_2 \cdot H_2O$

| Atom | Wyckoff | Occ | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|---|---|
| Er1 | 4e | 1 | 0.2550(5) | −0.1428(8) | −0.46235 (4) | 0.00687 (1) |
| K1 | 4e | 1 | −0.2095 (3) | −0.3318 (3) | −0.6860 (2) | 0.0210 (5) |
| S1 | 4e | 1 | 0.0521 (2) | −0.1364 (3) | −0.3185 (2) | 0.0082 (4) |
| S2 | 4e | 1 | 0.5035 (2) | −0.2022 (3) | −0.5991 (2) | 0.0083 (4) |
| O1 | 4e | 1 | −0.1021 (7) | −0.0636 (9) | −0.3876 (7) | 0.0147 (1) |
| O2 | 4e | 1 | 0.0789 (8) | −0.2153 (9) | −0.1806 (7) | 0.0166 (1) |
| O3 | 4e | 1 | 0.0620 (8) | −0.2563 (9) | −0.4221 (7) | 0.0157 (1) |
| O4 | 4e | 1 | 0.1691 (8) | −0.0128 (9) | −0.2924 (8) | 0.0177 (1) |
| O5 | 4e | 1 | 0.5923 (9) | −0.2828 (9) | −0.4567 (8) | 0.0192 (1) |
| O6 | 4e | 1 | 0.3700 (8) | −0.1181 (9) | −0.6068 (8) | 0.0162 (1) |
| O7 | 4e | 1 | 0.4477 (8) | −0.3217 (8) | −0.7221 (7) | 0.0131 (1) |
| O8 | 4e | 1 | 0.5980 (7) | −0.0870 (8) | −0.6272 (7) | 0.0130 (1) |
| $O9_W$ | 4e | 1 | 0.3292 (8) | −0.4206 (9) | −0.4461 (8) | 0.0159 (1) |
| H1A | 4e | 1 | 0.2577 | −0.4989 | −0.4836 | 0.019 |
| H1B | 4e | 1 | 0.4286 | −0.4470 | −0.4025 | 0.019 |

[a]Ueq is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor