Supporting Information

Ln₂(SeO₃)₂(SO₄)(H₂O)₂ (Ln=Sm, Dy, Yb): A Mixed-Ligand Pathway to New Lanthanide(III) Multifunctional Materials Featuring Nonlinear Optical and Magnetic Anisotropy Properties

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EXPERIMENTAL SECTION

Reagents. Thiophene-2-carbonyl chloride, aniline, KSeCN, Sm(NO₃)₃·6H₂O, Dy(NO₃)₃·6H₂O, Yb(NO₃)₃·5H₂O, HNO₃ (67 %), acetone, ethanol, dichloromethane.

Synthesis of C₁₂H₁₀N₂OSSe (TAS). The synthesis and characterization of TAS precursor have been reported by us.[1]

Synthesis of Ln₂(SeO₃)₂(SO₄)(H₂O)₂ (Ln = Sm, Dy, Yb). Ln(NO₃)₃·xH₂O [(Ln = Sm, Yb, x = 6; Ln = Dy, x = 5) (2 mmol)] was dissolved in 4 M HNO₃ (10 mL) in a 23 mL-PTFE-lined autoclave and TAS (2 mmol, 0.62 g) was added. The autoclave was heated at 200 °C for 60 h and cooled slowly to 25 °C at the rate of 5 °C/h. Sm₂(SeO₃)₂(SO₄)(H₂O)₂ and Dy₂(SeO₃)₂(SO₄)(H₂O)₂ were isolated as colorless crystals and Yb₂(SeO₃)₂(SO₄)(H₂O)₂ as white powder by filtration, and the samples were washed with deionized water and dried in air (Yield based on Ln: Sm₂(SeO₃)₂(SO₄)(H₂O)₂ 0.32 g, 46.6%, Dy₂(SeO₃)₂(SO₄)(H₂O)₂ 0.30 g, 42.2%, Yb₂(SeO₃)₂(SO₄)(H₂O)₂ 0.28 g, 38.2%) (Scheme S1).

Single-crystal X-ray diffraction. Single crystal crystallographic data of Sm₂(SeO₃)₂(SO₄)(H₂O)₂ (at 298 K), and Dy₂(SeO₃)₂(SO₄)(H₂O)₂ (at 299 K) were collected using a Bruker D8 Venture diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a Photon 2 detector. Data were collected using 0.5° oscillations of phi and omega. Data processing (SAINT) and scaling (SADABS) were performed using the Apex3 software system. The structure was solved by intrinsic phasing (SHELXT) and refined by full-matrix least-squares techniques on F² (SHELXL) using the SHELXTL software suite.[2] All non-hydrogen atoms were refined anisotropically (Figure S1). Hydrogen atoms attached to water molecules in Sm₂(SeO₃)₂(SO₄)(H₂O)₂, and Dy₂(SeO₃)₂(SO₄)(H₂O)₂ were identified from the difference electron density map and refined with appropriate distance fixing restraints. Crystal structures were viewed with VESTA.[3]

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) measurements on Sm₂(SeO₃)₂(SO₄)(H₂O)₂, Dy₂(SeO₃)₂(SO₄)(H₂O)₂, and Yb₂(SeO₃)₂(SO₄)(H₂O)₂ were performed using a Bruker D2 Phaser diffractometer with a LynxEye-XE-T detector. Data were collected in the 2θ range of 5 ° – 120 ° at 0.64 °/min. Rietveld refinement of the XRD pattern was performed using TOPAS Academic V6.

Thermal Analysis. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) measurements were performed using a TA SDT Q600 Instrument. Approximately 10 mg of Ln₂(SeO₃)₂(SO₄)(H₂O)₂ (Ln = Sm, Dy, Yb) were placed in an alumina crucible and heated at a rate of 20 °C/min from room temperature to 1000 °C under flowing nitrogen (flow rate: 100 mL/min) (Figure S1 – S3).

Infrared Spectroscopy. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra for Ln₂(SeO₃)₂(SO₄)(H₂O)₂ (Ln = Sm, Dy, Yb) were collected separately using a Shimadzu IR Affinity-1S in 500 to 4000 cm⁻¹ frequency range (Figure S4).

UV-Vis-NIR Spectroscopy. Optical reflectance was measured on Ln₂(SeO₃)₂(SO₄)(H₂O)₂ using the Universal Measurement (UMA) option of Agilent Cary UV-Vis (NIR) 7000
Spectrophotometer. A mixture of approximately 30 mg of each sample and 60 mg of PTFE was pelletized and used for the measurement (Figure S5).

**Second Harmonic Generation (SHG).** Powder SHG measurements were performed on a modified Kurtz-nonlinear optical system using a pulsed Nd:YAG laser with a wavelength of 1064 nm. A detailed description of the equipment and methodology has been published.[4] SHG response as a function of particle size was measured on Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ powder with the following particles sizes: 15±5, 32.5±12.5, 54±9, 69±6, 82.5±7.5, 107.5±17.5, and 137.5±12.5 µm. Relevant comparisons with known SHG α–SiO$_2$ material having a similar particle size range were made (Figure S6). No index matching fluid was used in any of the experiments.

**Magnetization and Specific Heat** (Figure S7 – S12). DC magnetization measurements on Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$, Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$, and Yb$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ powders were performed with the Vibrating sample magnetometer (VSM) option of Quantum Design Physical Properties Measurement System (PPMS). Magnetic susceptibility is defined as the ratio between the magnetization and the applied magnetic field: $\chi = \frac{M}{\mu_0 H}$. Heat capacity was measured using the PPMS, employing the semiadiabatic pulse technique from $T = 2$ K to 300 K.

**DFT Calculations.** Spin-polarized electronic structure calculations were performed using a full-potential linearized augmented plane wave method as implemented in the WIEN2k code.[5] The exchange and correlation energies were treated within the density functional theory (DFT) using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation.[6] For the Ln 4f localized electrons, a typical PBE0 onsite hybrid functionals ($\alpha = 0.25$) was adopted. The muffin-tin radius values of 2.00, 1.61, 1.32, 1.01 and 0.54 Bohr were used for the Ln (Dy, Sm or Yb), Se, S, O, and H atoms, respectively. The self-consistencies were carried out using a 5 × 4 × 5 k mesh in the irreducible Brillouin zone.

![Scheme S1. Synthesis of C$_{12}$H$_{10}$N$_2$OSSe (TAS) and Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ (Ln = Sm, Dy, Yb).](image)

**RESULTS AND DISCUSSION**

**Thermogravimetric Analysis.** The thermal behavior of Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure S2-S4). Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ compounds are stable up to $T \approx 200$ °C. From 200 °C < T < 350 °C, the mass reduction from Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ corresponds to the loss of two H$_2$O molecules. The experimental weight losses for Sm, Dy and Yb compounds are 5.4 %, 5.1 %, and
4.8 %, respectively, which are in good agreement with the calculated weight losses (5.24%, 5.06%, and 4.92%). This confirms that two H₂O molecules are chemically bonded to the Ln<sup>3+</sup> cation center. Further decomposition occurs at \( T \approx 670 \, ^{\circ}\text{C} – 890 \, ^{\circ}\text{C} \). This is attributed to the loss of 2Se and 2O₂ (Sm₂(SeO<sub>3</sub>)₂(SO₄)(H₂O): Exp. 31.8%, Cal. 32.32%; Dy₂(SeO₃)₂(SO₄)(H₂O): Exp. 30.8%, Cal. 31.21%; Yb₂(SeO₃)₂(SO₄)(H₂O): Exp. 29.4%, Cal. 30.31%).

Figure S1. Thermogravimetry (TG) and differential scanning calorimetry (DSC) of Sm₂(SeO₃)₂(SO₄)(H₂O)₂ showing the loss of 2H₂O molecules at \(~230 \, ^{\circ}\text{C}\) and decomposition at \(~670 \, ^{\circ}\text{C}\).
Figure S2. Thermogravimetry (TG) and differential scanning calorimetry (DSC) of Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ showing the loss of 2H$_2$O molecules at ~265 °C and decomposition at ~690 °C.
Figure S3. Thermogravimetry (TG) and differential scanning calorimetry (DSC) of Yb$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ showing the loss of 2H$_2$O molecules at ~200 °C and decomposition at ~650 °C.
**Infrared Spectroscopy.** To gain insight into the symmetry and local structure of ($\text{SeO}_3^{2-}$), ($\text{SO}_4^{2-}$), and H$_2$O building units, we performed infrared spectroscopic measurements on Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ powders (Figure S4). The bands at $\sim$600 cm$^{-1}$ are assigned to Ln-O stretching vibrations. The local symmetry of ($\text{SeO}_3^{2-}$) distorted trigonal pyramid is proved to have $C_s$ point group, $\Gamma_{\text{vib}} = 3A' + 3A''$. This is confirmed by the six peaks between 600 – 800 cm$^{-1}$. ($\text{SO}_4^{2-}$) approximate tetrahedra has pseudo-$T_d$ point symmetry, $\Gamma_{\text{vib}} = 3T_2$, as evidenced by the three peaks between 900 – 1200 cm$^{-1}$. H$_2$O ligand features 3 absorption bands in the IR spectra, consistent with $C_{2v}$ point group, $\Gamma_{\text{vib}} = 2A_1 + B_1$. The broad bands at $\sim$3475 cm$^{-1}$ and a band at $\sim$1640 cm$^{-1}$ correspond to the characteristic O-H stretching vibrations and H-O-H bending mode.
Figure S4. ATR-FTIR spectra of Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ (Ln = Sm, Dy, Yb) from 4000 cm$^{-1}$ – 500 cm$^{-1}$.
UV-Vis-NIR spectroscopy. To probe the interaction between the orbital \( L \) and spin angular momentum \( S \) (Russell-Saunders coupling or \( LS \) coupling) associated with the frontier \( 4f \) orbitals and electronic states of the \( \text{Ln}^{3+} \) complexes, we performed the UV-Vis-NIR reflectance measurements on \( \text{Ln}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2 \) powder samples. The data are expressed as the Kubelka-Munk function \( F(R) \) versus \( \hbar \nu \) (Figure S5a-c).\(^{[7]}\) Energy states for spin-allowed transitions between the ground state and the excited states for \( f^5 \) (Sm\(^{3+}\), \( ^6H_{5/2}, ^6H \) and \( ^6F \)), \( f^9 \) (Dy\(^{3+}\), \( ^6H_{15/2}, ^6H \) and \( ^6F \)), and \( f^{13} \) (Yb\(^{3+}\), \( ^2F_{7/2}, ^2F_{5/2} \)) systems are presented in Figure S5d-f, respectively. The electronic spectra of the materials proved the characteristics of strong spin-orbit \( (L+S) \) coupling of the \( \text{Ln}^{3+} \) cations and negligible ligand-field-induced splitting.\(^{[8]}\) Unlike the \( d \)-block transition elements, \( \text{Ln}^{3+} \) compounds display sharp absorption bands attributed to the weak overlap between the ‘buried’ \( f \)-orbitals of \( \text{Ln}^{3+} \) and the \( s \) and \( p \) orbitals of the ligands. Band assignments are consistent with the electronic transitions of other relevant \( \text{Ln}^{3+} \) systems and depicted in Figure S5.\(^{[9]}\)
Figure S5. (a-c) UV-Vis spectra for Sm$_2$(SeO$_2$)$_2$(SO$_4$)(H$_2$O)$_2$, Dy$_2$(SeO$_2$)$_2$(SO$_4$)(H$_2$O)$_2$, and Yb$_2$(SeO$_2$)$_2$(SO$_4$)(H$_2$O)$_2$ respectively showing characteristics of electronic transitions. (d-f) Energy states for spin-allowed transitions for $f^6$ (Sm$^{3+}$), $f^9$ (Dy$^{3+}$), and $f^{13}$ (Yb$^{3+}$) ions considering spin-orbit ($L+S$) coupling.$^{[8-9,9c-f]}$ All the compounds have a band at $-0.64$ eV which cannot be accounted for by the conventional $f^5-f^6$ transition. This band is likely due to ligand stimulated Ln$^{3+}$ photosensitized emission.$^{[10]}$
Figure S6. SHG intensities of Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ (Ln = Sm, Dy, Yb) with α-SiO$_2$ as reference.
Figure S7. (a) Magnetic susceptibility of Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ from $T = 2$ K – 10 K at $\mu_0H = 0.1$ T and $\mu_0H = 7$ T. (b) First derivative of magnetization as a function of temperature $dM/dT$ versus temperature for Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$.

Figure S8. (a) Magnetic susceptibility of Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ from $T = 2$ K – 10 K at $\mu_0H = 0.1$ T and $\mu_0H = 7$ T. (b) First derivative of magnetization as a function of temperature $dM/dT$ versus temperature for Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ at $\mu_0H = 7$ T.
Figure S9. (a) Magnetic susceptibility of $\text{Yb}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ from $T = 2 \text{ K} - 10 \text{ K}$ at $\mu_0H = 0.1 \text{ T}$ and $\mu_0H = 7 \text{ T}$. (b) $dM/dT$ versus temperature for $\text{Yb}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ from $T = 2 \text{ K} - 10 \text{ K}$ at $\mu_0H = 0.1 \text{ T}$ and $\mu_0H = 7 \text{ T}$.

Figure S10. Molar heat capacity over cubic temperature ($C_p/T^3$) versus temperature for $\text{Sm}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$. The bump at $\sim 16 \text{ K}$ indicates the presence of the Einstein vibration mode.
Figure S11. $C_p/T^3$ versus $T$ for Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$. The signature of the Einstein vibration mode is overwhelmed by the Schottky anomaly.

Figure S12. $C_p/T^3$ versus $T$ for Yb$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$. The signature of the Einstein vibration mode also appear at $\sim$16 K.
Table S1. Crystallographic data of Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$, and Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ as obtained by single-crystal XRD.

|                      | Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ | Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ |
|----------------------|----------------------------------------|---------------------------------------|
| **Formula**          | Sm$_2$Se$_2$SO$_{12}$H$_4$             | Dy$_2$Se$_2$SO$_{12}$H$_4$            |
| **M (g mol$^{-1}$)** | 686.71                                 | 711.01                                |
| **T (K)**            | 298                                    | 299                                   |
| **X-ray radiation**  | MoK$\alpha$                           | MoK$\alpha$                          |
| **$\lambda$ (Å)**    | 0.71073                                | 0.71073                               |
| **Crystal system**   | Monoclinic                             | Monoclinic                            |
| **Space group**      | C2                                     | C2                                    |
| **Z**                | 2                                      | 2                                     |
| **a (Å)**            | 11.8620(5)                             | 11.751(3)                             |
| **b (Å)**            | 6.9490(3)                              | 6.8674(16)                            |
| **c (Å)**            | 6.6063(3)                              | 6.5245(18)                            |
| **$\beta$ (°)**     | 103.413(2)                             | 103.124(13)                           |
| **$V$(Å$^3$)**       | 529.70(4)                              | 512.8(2)                              |
| **$\rho_{\text{calc}}$ (g cm$^{-1}$)** | 4.306                                 | 4.605                                 |
| **Reflns collected/unique/obs** | 4293 / 1111 / 1103 | 6902 / 1222 / 1222 |
| **No. of parameters** | 84                                     | 85                                    |
| **$\mu$ (mm$^{-1}$)** | 18.103                                 | 21.821                                |
| **2$\theta_{\text{max}}$ (°)** | 55.0                                   | 56.6                                  |
| **GOF**              | 1.111                                  | 1.134                                 |
| **$R(F)$**$^a$       | 0.0196                                 | 0.0226                                |
| **$R_w(F^2)$**$^b$   | 0.0536                                 | 0.0586                                |
| **Flack parameter**  | 0.096(16)                              | 0.18(5)                               |

$^a$R($F$) = $\sum$ ||$F_0$|| - 1/$F_0^2$/$\sum$ ||$F_0$|| \quad (1)

$^b$R$_w$(F$^2$) = [$\sum$ $w$ ($F_0^2$ - $F_o^2$)$^2$/$\sum$ $w(F_0^2)^2$]$^{1/2}$ \quad (2)
Table S2. Crystal structure information and refinement parameters for Ln$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ (Ln = Sm, Dy, Yb) at $T = 298$ K obtained by Rietveld refinement of powder XRD patterns.

| Parameter                      | Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ | Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ | Yb$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ |
|--------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| Formula weight                 | 686.71                                | 711.01                                | 732.09                                |
| Temperature (K)                | 298                                   | 298                                   | 298                                   |
| X-ray radiation                | Cu Kα                                 | Cu Kα                                 | Cu Kα                                 |
| Wavelength (Å)                 | 1.5406                                | 1.5406                                | 1.5406                                |
| Crystal system                 | Monoclinic                            | Monoclinic                            | Monoclinic                            |
| Space group                    | C2                                    | C2                                    | C2                                    |
| $Z$                            | 2                                     | 2                                     | 2                                     |
| $a$ (Å)                        | 11.859(2)                             | 11.721(2)                             | 11.595(2)                             |
| $b$ (Å)                        | 6.961(3)                              | 6.856(2)                              | 6.778(2)                              |
| $c$ (Å)                        | 6.596(2)                              | 6.508(2)                              | 6.425(3)                              |
| $\alpha = \gamma$ (°)         | 90                                    | 90                                    | 90                                    |
| $\beta$ (°)                   | 103.334(2)                            | 103.093(2)                            | 103.023(6)                            |
| $V$ (Å$^3$)                    | 529.82(6)                             | 509.38(4)                             | 491.95(6)                             |
| $\rho_{calc}$ (g/cm$^3$)       | 4.304                                 | 4.635                                 | 4.942                                 |
| $2\theta$ (°)                 | 5 – 120                               | 5 – 120                               | 5 – 120                               |
| $R$-factor (%)                 | $R_p^a = 7.7$, $R_{wp}^b = 14.8$, $R_{exp}^c = 6.2$ | $R_p^a = 5.6$, $R_{wp}^b = 13.7$, $R_{exp}^c = 3.8$ | $R_p^a = 5.2$, $R_{wp}^b = 10.2$, $R_{exp}^c = 5.8$ |

\[ aR_p = \frac{\sum_l^n |Y_l^{obs} - Y_l^{calc}|}{\sum_l^n Y_l^{obs}} \times 100\% \] (3)

\[ bR_p = \frac{\sum_l^n \left( \frac{w_l(Y_l^{obs} - Y_l^{calc})^2}{\sum_l^n Y_l^{obs}} \right)^{\frac{1}{2}}}{\sum_l^n w_l Y_l^{obs}} \times 100\% \] (4)

\[ cR_{exp} = \frac{\sum_l^n w_l (Y_l^{obs} - Y_l^{calc})^2}{\sum_l^n w_l (Y_l^{obs})^2}^{\frac{1}{2}} \times 100\% \] (5)
Table S3. Crystallographic data of Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ as obtained by single-crystal XRD at $T = 100$ K.

|                           | Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ |
|---------------------------|----------------------------------------|
| Formula                   | Dy$_2$Se$_2$SO$_4$H$_4$                |
| $M$ (g mol$^{-1}$)        | 711.01                                 |
| $T$ (K)                   | 100                                    |
| X-ray radiation           | MoK$\alpha$                            |
| $\lambda$ (Å)             | 0.71073                                |
| Crystal system            | Monoclinic                             |
| Space group               | C2                                     |
| $Z$                       | 2                                      |
| $a$ (Å)                   | 11.7017(9)                             |
| $b$ (Å)                   | 6.8397(5)                              |
| $c$ (Å)                   | 6.4997(5)                              |
| $\alpha$ ($^\circ$)       | 90                                     |
| $\beta$ ($^\circ$)        | 103.198(3)                             |
| $\gamma$ ($^\circ$)       | 90                                     |
| $V$ (Å$^3$)               | 506.47(7)                              |
| $\rho_{calc}$ (g cm$^{-1}$) | 4.662                                  |
| No. of reflections        | 2544                                   |
| No. of parameters         | 86                                     |
| $\mu$ (mm$^{-1}$)         | 22.092                                 |
| $2\theta_{max}$ ($^\circ$)| 53.0                                   |
| GOF                       | 1.128                                  |
| $R(F)$                    | 0.0251                                 |
| $R(F_{o}^{2})$            | 0.0675                                 |
| Flack parameter           | 0.22(6)                                |

\[ R(F) = \frac{\sum |F_o| - |F_o|^2}{\sum |F_o|} \]  \hspace{1cm} (1)

\[ R_w(F_o^2) = \left[\frac{\sum w(F_o^2 - F_o^2)^2}{\sum w(F_o^2)^2}\right]^{1/2} \]  \hspace{1cm} (2)
**Table S4.** Atomic positions for Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ obtained from single-crystal XRD at $T = 298$ K.

| Element | $x$          | $y$        | $z$          | $U$(Å$^2$)   |
|---------|--------------|------------|--------------|--------------|
| Sm      | 0.80282(3)   | 0.43369(7) | 0.14583(5)   | 0.00843(14)  |
| Se      | 0.71023(7)   | 0.4463(2)  | 0.63710(12)  | 0.0156(2)    |
| S       | 0.5000       | 0.5867(5)  | 0.0000       | 0.0139(6)    |
| O1      | 0.8121(5)    | 0.4291(17) | 0.5049(8)    | 0.0171(11)   |
| O2      | 0.7679(8)    | 0.6160(12) | 0.8146(14)   | 0.0164(19)   |
| O3      | 0.7409(9)    | 0.2659(12) | 0.8106(14)   | 0.0198(19)   |
| O4      | 0.5952(5)    | 0.4588(13) | 0.1089(11)   | 0.0204(17)   |
| O5      | 0.4609(8)    | 0.7077(13) | 0.1508(15)   | 0.030(2)     |
| O6W     | 0.5137(7)    | 0.1038(12) | -0.2478(15)  | 0.0276(18)   |
| H6A     | 0.567(8)     | 0.144(19)  | -0.302(17)   | 0.033        |
| H6B     | 0.452(6)     | 0.060(19)  | -0.326(16)   | 0.033        |

**Table S5.** Atomic positions for Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ obtained from single-crystal XRD at $T = 299$ K.

| Element | $x$          | $y$        | $z$          | $U$(Å$^2$)   |
|---------|--------------|------------|--------------|--------------|
| Dy      | 0.19910(3)   | 0.56613(12)| 0.85558(5)   | 0.00808(15)  |
| Se      | 0.28906(9)   | 0.5578(5)  | 0.36306(15)  | 0.0201(3)    |
| S       | 0.5000       | 0.4055(5)  | 0.0000       | 0.0131(7)    |
| O1      | 0.1863(6)    | 0.567(3)   | 0.4984(9)    | 0.0159(12)   |
| O2      | 0.2328(11)   | 0.3808(18) | 0.1830(18)   | 0.017(2)     |
| O3      | 0.2556(11)   | 0.7335(19) | 0.187(2)     | 0.021(3)     |
| O4      | 0.4036(7)    | 0.539(2)   | 0.8919(15)   | 0.023(3)     |
| O5      | 0.5399(10)   | 0.2850(17) | 0.846(2)     | 0.029(3)     |
| O6W     | 0.4803(9)    | 0.8930(17) | 1.248(2)     | 0.030(3)     |
| H6A     | 0.462(14)    | 0.786(16)  | 1.29(3)      | 0.036        |
| H6B     | 0.550(7)     | 0.93(2)    | 1.31(3)      | 0.036        |
**Table S6.** Atomic positions for Yb$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ obtained from powder XRD.

|     | x       | y       | z       | B (Å$^2$) |
|-----|---------|---------|---------|-----------|
| Yb  | 0.20655(3) | 0.58071(13) | 0.86228(5) | 2.74(8)  |
| Se  | 0.2831(8)  | 0.5454(4)  | 0.3534(15) | 2.66(2)  |
| S   | 0.5000    | 0.4290(5)  | 0.0000    | 1.42(7)  |
| O1  | 0.1863(6)  | 0.567(3)   | 0.4984(9)  | 3.59(12) |
| O2  | 0.2328(11) | 0.3808(18) | 0.1830(18) | 4.25(3)  |
| O3  | 0.2556(11) | 0.7335(19) | 0.187(2)   | 3.99(3)  |
| O4  | 0.4036(7)  | 0.539(2)   | 0.8919(15) | 4.23(3)  |
| O5  | 0.5399(10) | 0.2850(17) | 0.846(2)   | 3.65(3)  |
| O6W | 0.4803(9)  | 0.8930(17) | 1.248(2)   | 4.35(2)  |
| H6A | 0.462(14)  | 0.786(16)  | 1.29(3)    | 4.35(2)  |
| H6B | 0.550(7)   | 0.93(2)    | 1.31(3)    | 4.35(2)  |

**Table S7.** Bond lengths (Å) of Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ obtained from single-crystal XRD.

|            |        |        |        |
|------------|--------|--------|--------|
| Sm-O1      | 2.349(6) | Se-O1  | 1.651(5) |
| Sm-O2      | 2.398(8) | Se-O3  | 1.681(9) |
| Sm-O3      | 2.398(9) | Se-O2  | 1.692(9) |
| Sm-O4      | 2.424(6) | S-O5   | 1.459(8) |
| Sm-O6W     | 2.430(8) | S-O5   | 1.459(8) |
| Sm-O5      | 2.440(8) | S-O4   | 1.485(8) |
| Sm-O3      | 2.460(9) | S-O4   | 1.485(8) |
| Sm-O2      | 2.478(9) |        |         |

**Table S8.** Bond lengths (Å) of Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ obtained from single-crystal XRD.

|            |        |        |        |
|------------|--------|--------|--------|
| Dy-O1      | 2.301(6) | Se-O1  | 1.651(6) |
| Dy-O2      | 2.338(12) | Se-O3 | 1.650(14) |
| Dy-O3      | 2.376(13) | Se-O2  | 1.715(13) |
| Dy-O4      | 2.368(8)  | S-O5   | 1.458(11) |
| Dy-O6W     | 2.380(10) | S-O5   | 1.458(11) |
| Dy-O5      | 2.390(11) | S-O4   | 1.503(11) |
| Dy-O3      | 2.407(13) | S-O4   | 1.503(11) |
| Dy-O2      | 2.441(12) |        |         |
**Table S8.** Bond lengths (Å) of Yb$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$ obtained from powder XRD.

|          | Yb-O1   | Yb-O3   | Yb-O2   | Yb-O4   | Yb-O6W  | Yb-O5   | Yb-O3   | Yb-O2   |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|
| Yb-O1    | 2.298(6)| 2.428(13)| 2.193(13)| 2.267(9)| 2.474(11)| 2.360(12)| 2.283(13)| 2.427(12)|
| Se-O1    | 1.619(12)| 1.648(13)| 1.580(12)| 1.438(14)| 1.438(14)| 1.483(11)| 1.483(11)|

**Table S9.** Calculated bond valence sum ($V_i$) for Sm$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$.[11]

|          | O1       | O2       | O3       | O4       | O5       | O6W      | $V_i$ = $\sum S_{ij}$ |
|----------|----------|----------|----------|----------|----------|----------|-----------------------|
| Sm       | R$_{ij}$ | 2.349(6) | 2.398(9), 2.478(9) | 2.398(9), 2.460(9) | 2.424(6) | 2.440(8) | 2.430(8) |
| S        | S$_{ij}$ | 0.4518   | 0.3957, 0.3188 | 0.3957, 0.3347 | 0.3689   | 0.3533   | 0.3629, 2.982 |
| Se       | R$_{ij}$ | 1.651(5) | 1.692(9) | 1.681(9) |          |          | 4.341     |
| S        | S$_{ij}$ | 1.5410   | 1.3794   | 1.4210   |          | 1.485(8), 1.485(8) | 1.459(8), 1.459(8) |
|          |   S$_{ij}$ | 1.4560, 1.4560 | 1.5620, 1.5620 | 6.036     |

**Table S10.** Calculated bond valence sum ($V_i$) for Dy$_2$(SeO$_3$)$_2$(SO$_4$)(H$_2$O)$_2$.[11]

|          | O1       | O2       | O3       | O4       | O5       | O6W      | $V_i$ = $\sum S_{ij}$ |
|----------|----------|----------|----------|----------|----------|----------|-----------------------|
| Dy       | R$_{ij}$ | 2.301(6) | 2.338(12), 2.441(12) | 2.376(13), 2.407(13) | 2.368(8) | 2.390(11) | 2.380(10) |
| S        | S$_{ij}$ | 0.4445   | 0.4022, 0.3045 | 0.3629, 0.3338 | 0.3709   | 0.3495   | 0.3590, 2.927 |
| Se       | R$_{ij}$ | 1.651(6) | 1.715(13) | 1.650(14) |          |          | 4.382     |
| S        | S$_{ij}$ | 1.5410   | 1.2962   | 1.5452   |          | 1.503(11), 1.503(11) | 1.458(11), 1.458(11) |
|          |   S$_{ij}$ | 1.3868, 1.3868 | 1.5662, 1.5662 | 5.906     |
**Table S11.** Calculated bond valence sum ($V_i$) for $\text{Yb}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$.\textsuperscript{[11]}

|     | O1       | O2       | O3       | O4       | O5       | O6W      | $V_i = \sum S_{ij}$ |
|-----|----------|----------|----------|----------|----------|----------|---------------------|
| Yb  | 2.298(6) | 2.193(13), 2.427(12) | 2.428(13), 2.283(13) | 2.267(9) | 2.360(12) | 2.474(11) |                     |
| S$\text{ij}$ | 0.3947   | 0.5242, 0.2785 | 0.2777, 0.4110 | 0.4292 | 0.3338 | 0.2466 | 2.857 |
| Se  | 1.619(12) | 1.580(12) | 1.648(13) |          |          |          |                     |
| S   | 1.6802   | 1.8670   | 1.5536   |          |          |          | 5.101              |
| S$\text{ij}$ |          |          |          | 1.483(11), 1.483(11) | 1.438(14), 1.438(14) |          |                     |

**Table S12.** Debye and Einstein temperatures, $\theta_D$, $\theta_{E1}$, $\theta_{E2}$, and oscillator strengths, $s_D$, $s_{E1}$, $s_{E2}$ obtained from the analysis of phonons from the molar heat capacity over temperature ($C_p/T$) versus temperature ($T$) of $\text{Ln}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ ($\text{Ln} = \text{Sm, Dy, Yb}$).

| Material | $\theta_D$ (K) | $\theta_{E1}$ (K) | $\theta_{E2}$ (K) | $s_D$ | $s_{E1}$ | $s_{E2}$ |
|----------|----------------|-------------------|-------------------|-------|---------|---------|
| $\text{Sm}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ | 721(23) | 73(2) | 179(4) | 9.38(19) | 1.43(11) | 5.25(14) |
| $\text{Dy}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ | 654(23) | 62(3) | 163(5) | 9.04(2) | 1.00(10) | 4.71(16) |
| $\text{Yb}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ | 792(24) | 78(2) | 195(4) | 10.31(21) | 1.20(9) | 5.09(13) |

**Table S13.** Resulting $\beta_3$ (J mol$^{-1}$ K$^{-4}$) lattice vibration and $A$ (J K mol$^{-1}$) Schottky parameter parameters obtained from the analysis of Schottky anomalies in $C_p/T$ versus $T$ of $\text{Ln}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ ($\text{Ln} = \text{Sm, Dy, Yb}$).

| Material                  | $\beta_3$ (J mol$^{-1}$ K$^{-4}$) | $A$ (J K mol$^{-1}$) |
|---------------------------|----------------------------------|----------------------|
| $\text{Sm}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ | 0.00160(3)                      | 0.200(14)            |
| $\text{Dy}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ | 0.00196(19)                     | 19.3(6)              |
| $\text{Yb}_2(\text{SeO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ | 0.00109(1)                      | 0.370(8)             |
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