

Syntheses, Crystal Structures and SHG Properties of a Series of Polar Alkali-metal Molybdenum(VI) Selenites Based on Strandberg-type $[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ Polyanion

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Supporting Materials

Table S1. The configuration of the Mo and the orientation of the Se—Se vectors to the Mo rings in $[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ of different compounds.

Table S2. Direction and magnitude of the MoO_6 octahedra in the four compounds.

Table S3. Hydrogen bond distances (Å) and angles ($^\circ$) for $\alpha\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **2**.

Table S4. The local dipole moments for the SeO_3 groups, MoO_6 octahedra, $[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ anions and the net dipole moment within a unit cell for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **1**, $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **4**.

Figure S1. Simulated and measured XRD powder patterns for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **1**, $\alpha\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **2**, $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **4**.

Figure S2. DSC curves for $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **4**.

Figure S3. IR spectra for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **1**, $\alpha\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **2**, $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **4**.

Figure S4. UV-Visible absorption spectra for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **1**,

α -Rb₄Mo₅O₁₅(SeO₃)₂·(H₂O)₂ **2**, β -Rb₄Mo₅O₁₅(SeO₃)₂·(H₂O)₂ **3** and
K₄Mo₅O₁₅(SeO₃)₂·(H₂O)₂ **4**.

Figure S5. Optical diffuse reflectance spectra for HRb₃(Mo₅O₁₅)(SeO₃)₂(H₂O)₂ **1**,
 α -Rb₄Mo₅O₁₅(SeO₃)₂·(H₂O)₂ **2**, β -Rb₄Mo₅O₁₅(SeO₃)₂(H₂O)₂ **3** and
K₄Mo₅O₁₅(SeO₃)₂(H₂O)₂ **4**.

Figure S6. View of the structure of polyanion [Mo₅O₁₅(SeO₃)]²⁻ with the macroscopic
polarity indicated by small green arrows: viewed from above the Mo₅ ring (a) and
along the C₂ axis in the plane of the Mo₅ ring (b). MoO₆ octahedra are shaded in blue,
Rb, Se and O atoms are drawn as green, pink and red circles, respectively.

Table S1. The configuration of the Mo and the orientation of the Se—Se vectors to the Mo rings in $[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ of different compounds.

Polyanions	Deviation of the Mo5 ring/ $\times \text{Å}$						Angles/($^\circ$)	
	Mo1	Mo2	Mo3	Mo4	Mo5	Se1		Se2
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ in 1	0.172	0.200	0.154	0.045	0.081	2.134	2.098	89.9
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ in 2	0.044	0.191	0.101	0.170	0.217	2.129	2.130	88.6
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ I in 3	0	0.173	0.261	0.173	0.261	2.114	2.114	89.6
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ II in 3	0.154	0.230	0	0.154	0.230	2.125	2.125	89.2
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ I in 4	0	0.167	0.252	0.167	0.252	2.111	2.111	89.5
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ II in 4	0.149	0.223	0	0.149	0.223	2.120	2.120	89.9
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ in K₃Na *	0.206	0.179	0.048	0.166	0.091	2.109	2.132	90.0

*K₃Na is the abbreviation of K₃NaMo₅O₁₅(SeO₃)₂(H₂O)₂ in reference 12e.

Table S2. Direction and magnitude of the MoO₆ octahedra in the four compounds.

compound	MoO ₆ octahedron	distortion direction	Δ_d
HRb ₃ (Mo ₅ O ₁₅)(SeO ₃) ₂ (H ₂ O) ₂	Mo(1)O ₆	C ₂	1.49
	Mo(2)O ₆	C ₂	1.29
	Mo(3)O ₆	C ₂	1.46
	Mo(4)O ₆	C ₂	1.37
	Mo(5)O ₆	C ₂	1.27
α -Rb ₄ Mo ₅ O ₁₅ (SeO ₃) ₂ (H ₂ O) ₂	Mo(1)O ₆	C ₂	1.19
	Mo(2)O ₆	C ₂	1.22
	Mo(3)O ₆	C ₂	1.24
	Mo(4)O ₆	C ₂	1.20
	Mo(5)O ₆	C ₂	1.24
β -Rb ₄ Mo ₅ O ₁₅ (SeO ₃) ₂ (H ₂ O) ₂	Mo(1)O ₆	C ₂	1.29
	Mo(2)O ₆	C ₂	1.15
	Mo(3)O ₆	C ₂	1.20
	Mo(4)O ₆	C ₂	1.19
	Mo(5)O ₆	C ₂	1.26
	Mo(6)O ₆	C ₂	1.25
K ₄ Mo ₅ O ₁₅ (SeO ₃) ₂ (H ₂ O) ₂	Mo(1)O ₆	C ₂	1.33
	Mo(2)O ₆	C ₂	1.17
	Mo(3)O ₆	C ₂	1.21
	Mo(4)O ₆	C ₂	1.21
	Mo(5)O ₆	C ₂	1.25
	Mo(6)O ₆	C ₂	1.28

Table S3. Hydrogen bond distances (Å) and angles (°) for α -Rb₄Mo₅O₁₅(SeO₃)₂(H₂O)₂ **2**.

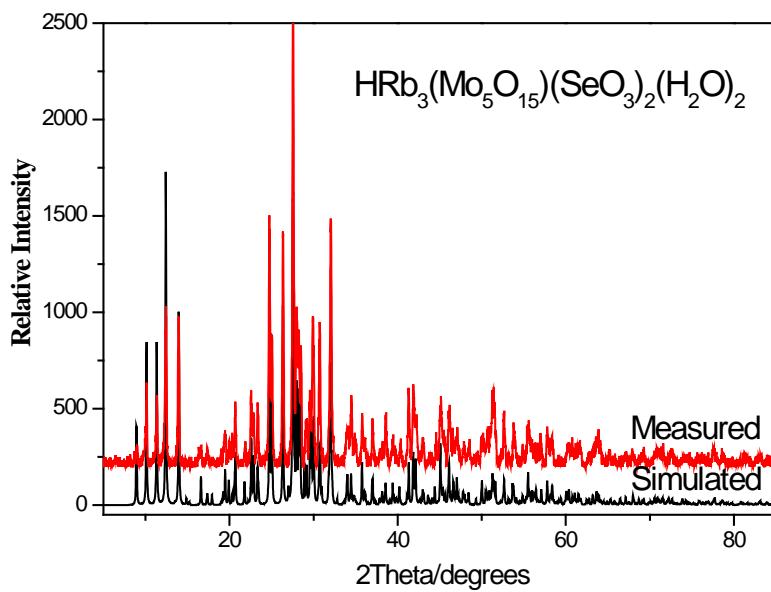
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
α -Rb ₄ Mo ₅ O ₁₅ (SeO ₃) ₂ ·(H ₂ O) ₂ 2				
O(1W)-H(1WA)...O(19)#1	0.85	2.16	2.872(5)	141.7
O(1W)-H(1WB)...O(1)#2	0.85	2.29	2.851(5)	124.0

Symmetry transformations used to generate equivalent atoms:

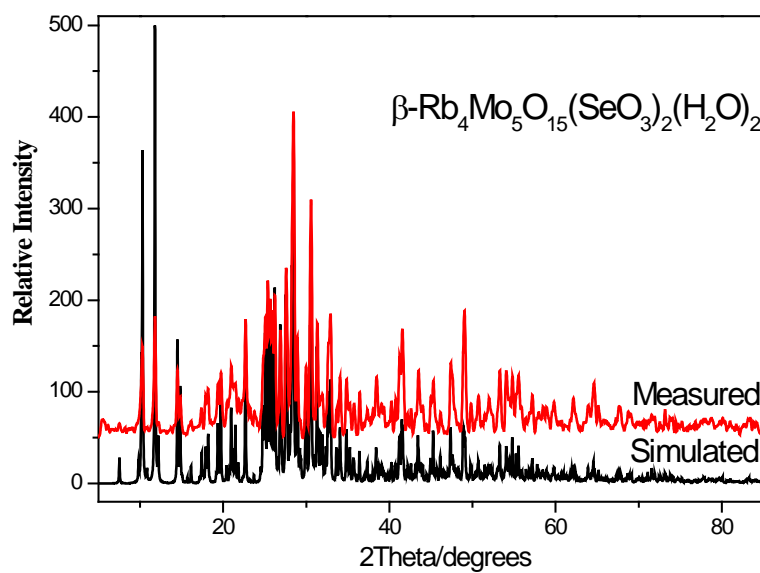
α -Rb₄Mo₅O₁₅(SeO₃)₂(H₂O)₂: #1 $x+1/2, -y+1/2, z+1/2$; #2 $x, y, z-1$.

Table S4. The local dipole moments for the SeO_3 groups, MoO_6 octahedra, $[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$ anions and the net dipole moment within a unit cell for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **1**, $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **4**.

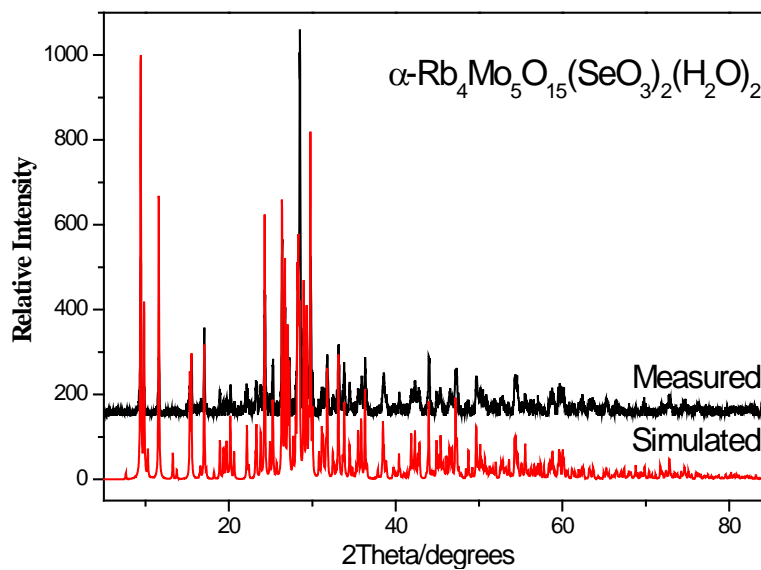
$\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ 1				
Polar unit	Dipole moment (D)			
	total magnitude	x-component	y-component	z-component
Se(1) O_3	8.79	7.91	0.55	3.80
Se(2) O_3	8.75	8.61	0.70	1.40
Mo(1) O_6	7.53	2.60	3.60	6.09
Mo(2) O_6	5.12	1.79	2.67	3.98
Mo(3) O_6	6.69	2.38	6.25	0.21
Mo(4) O_6	5.55	1.36	1.45	5.19
Mo(5) O_6	5.31	1.53	2.93	4.16
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)]^{2-}$	11.64	-9.30	5.14	-4.74
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	7.62	-0.69	4.44	-6.15
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	7.62	0.69	4.44	-6.15
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	7.62	0.69	-4.44	-6.15
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	7.62	-0.69	-4.44	-6.15
Net dipole moment (a unit cell)	24.60	0	0	24.60
$\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ 3				
Polar unit	Dipole moment (D)			
	total magnitude	x-component	y-component	z-component
Se(1) O_3	8.55	0.97	2.97	7.96
Se(2) O_3	8.66	0.21	3.23	8.03
Mo(1) O_6	6.24	0	6.24	0
Mo(2) O_6	5.42	4.29	1.31	3.04
Mo(3) O_6	5.12	0.56	4.71	1.93
Mo(4) O_6	5.06	0.31	4.67	1.90
Mo(5) O_6	5.94	5.06	1.98	2.40
Mo(6) O_6	6.59	0	6.59	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)]^{2-}$	8.28	-0.21	2.024	-8.03
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)]^{2-}$	8.77	-0.97	-3.54	7.96
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	6.52	0	-6.52	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	6.52	0	-6.52	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	5.25	0	5.25	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	5.25	0	5.25	0
Net dipole moment (a unit cell)	2.53	0	-2.53	0
$\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ 4				
Polar unit	Dipole moment (D)			
	total magnitude	x-component	y-component	z-component
Se(1) O_3	8.55	0.23	3.23	7.96
Se(2) O_3	8.25	0.89	2.90	7.67
Mo(1) O_6	6.20	0	6.20	0
Mo(2) O_6	5.44	4.40	1.21	2.96
Mo(3) O_6	5.34	0.84	4.85	2.07
Mo(4) O_6	6.48	0	6.48	0
Mo(5) O_6	5.92	5.20	1.72	2.26
Mo(6) O_6	5.08	0.52	4.46	2.37
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)]^{2-}$	8.23	-0.23	2.24	-7.92
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)]^{2-}$	8.70	0.89	-4.00	-7.67
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	5.47	0	5.47	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	5.47	0	5.47	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	6.90	0	-6.90	0
$[\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2]^{4-}$	6.90	0	-6.90	0
Net dipole moment (a unit cell)	2.87	0	-2.87	0



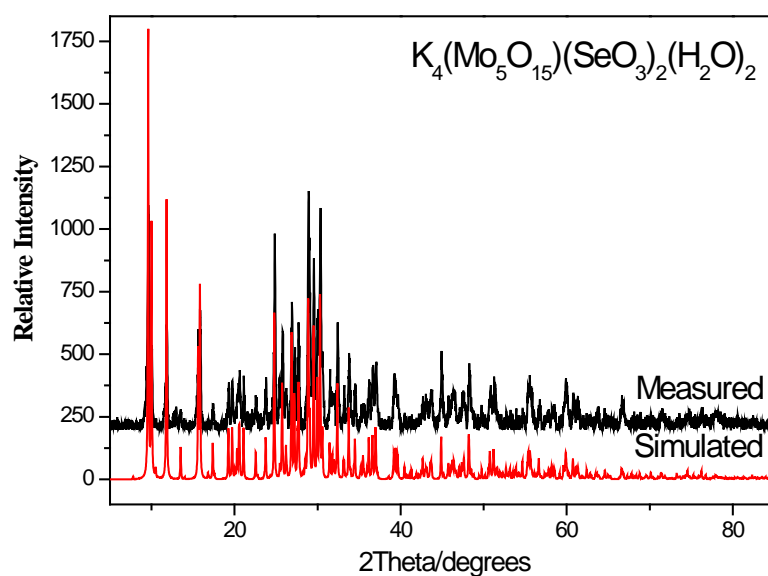
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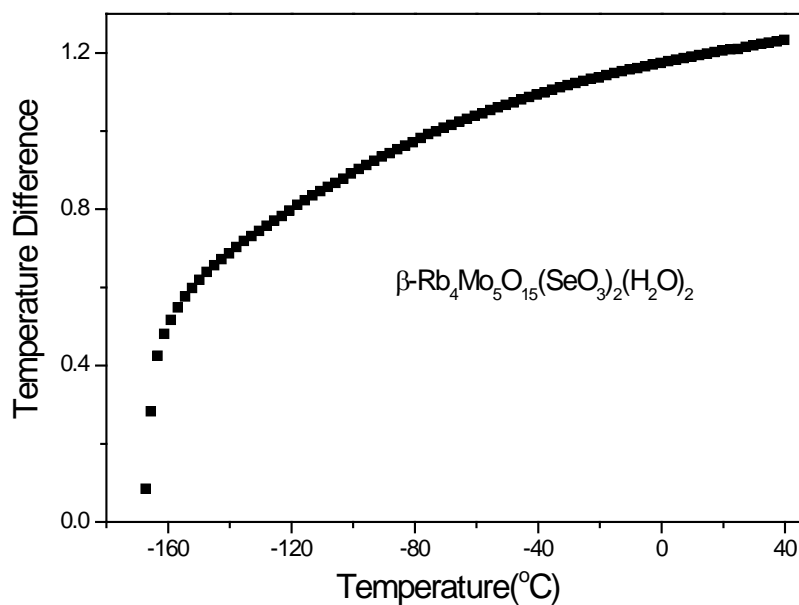


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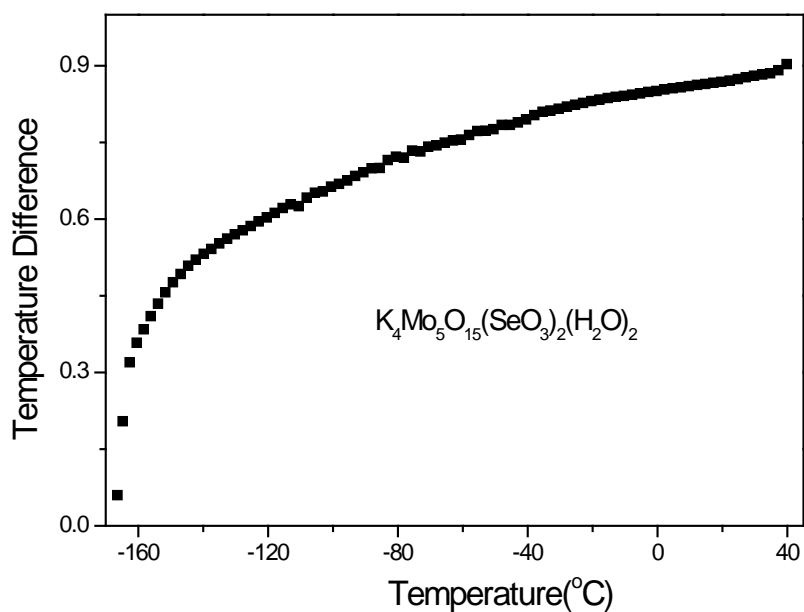


(d)

Figure S1. Simulated and measured XRD powder patterns for $HRb_3(Mo_5O_{15})(SeO_3)_2(H_2O)_2$ **1**, $\alpha-Rb_4Mo_5O_{15}(SeO_3)_2(H_2O)_2$ **2**, $\beta-Rb_4Mo_5O_{15}(SeO_3)_2(H_2O)_2$ **3** and $K_4Mo_5O_{15}(SeO_3)_2(H_2O)_2$ **4**.

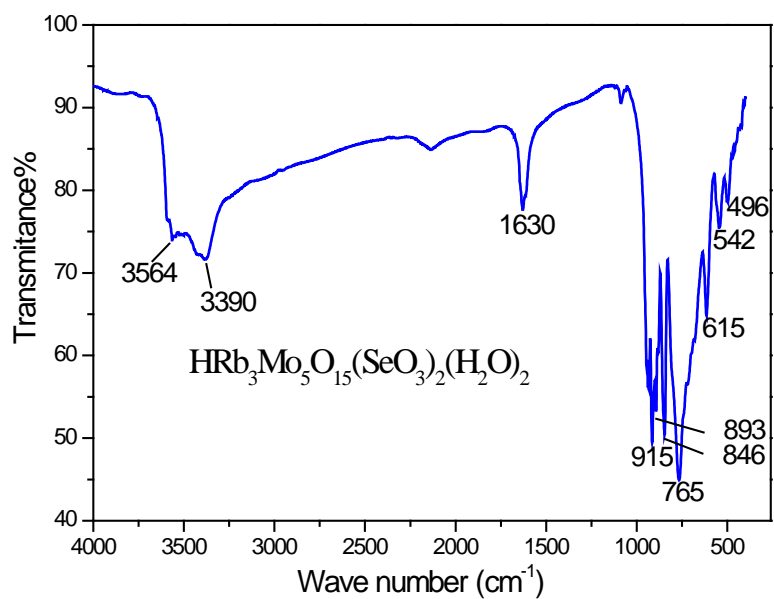


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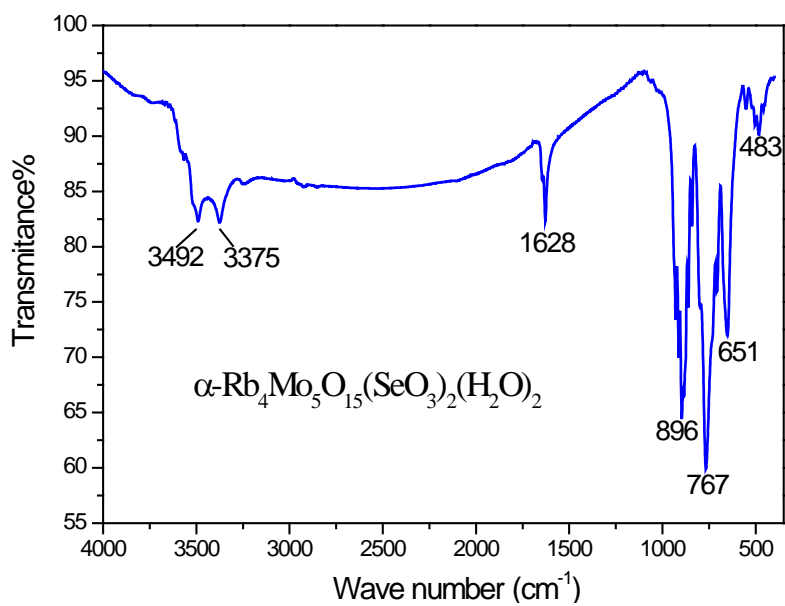


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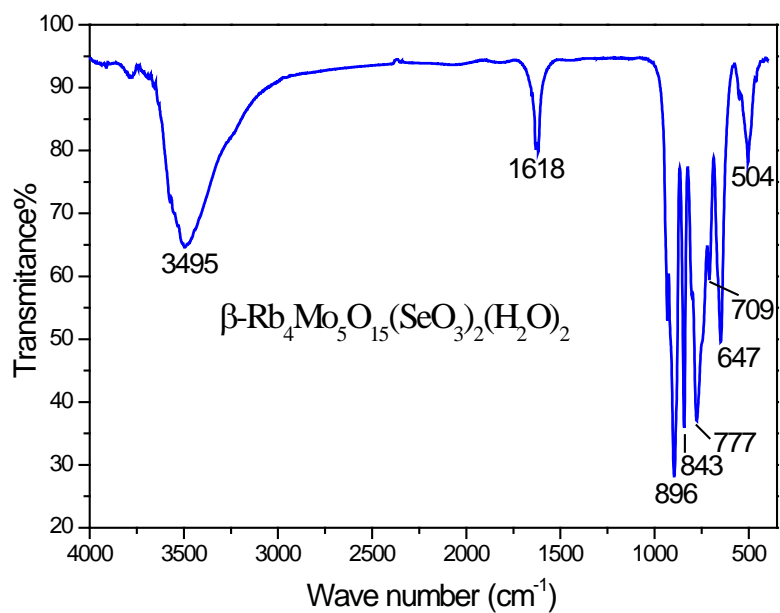
Figure S2. DSC curves for β - $Rb_4Mo_5O_{15}(SeO_3)_2 \cdot (H_2O)_2$ **3** and $K_4Mo_5O_{15}(SeO_3)_2 \cdot (H_2O)_2$ **4**.



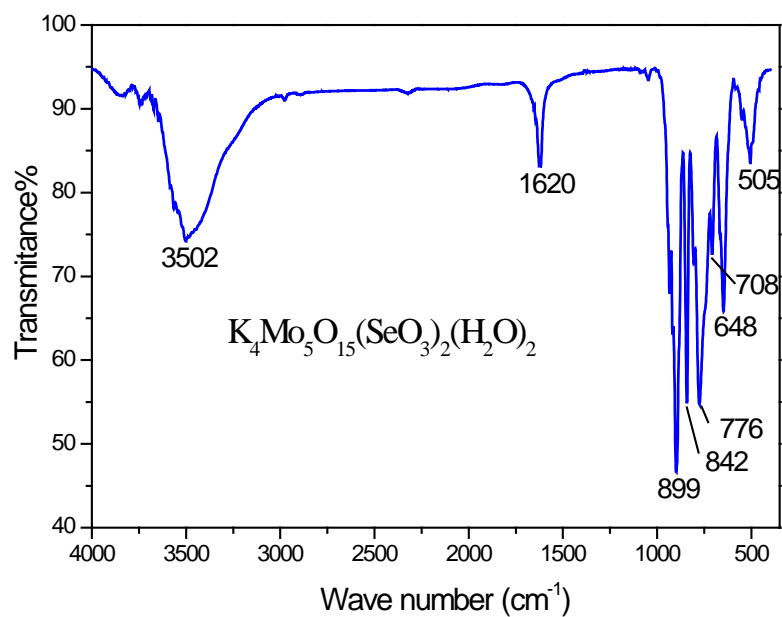
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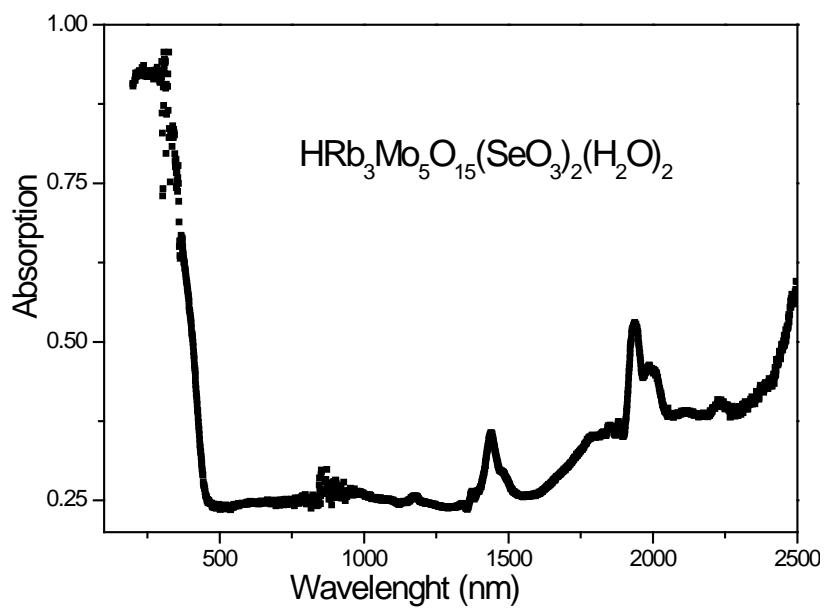


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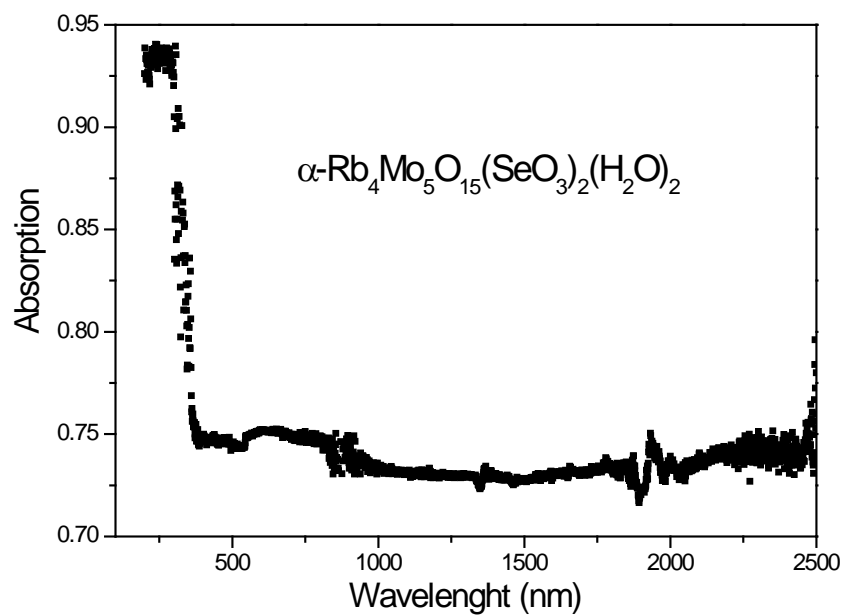


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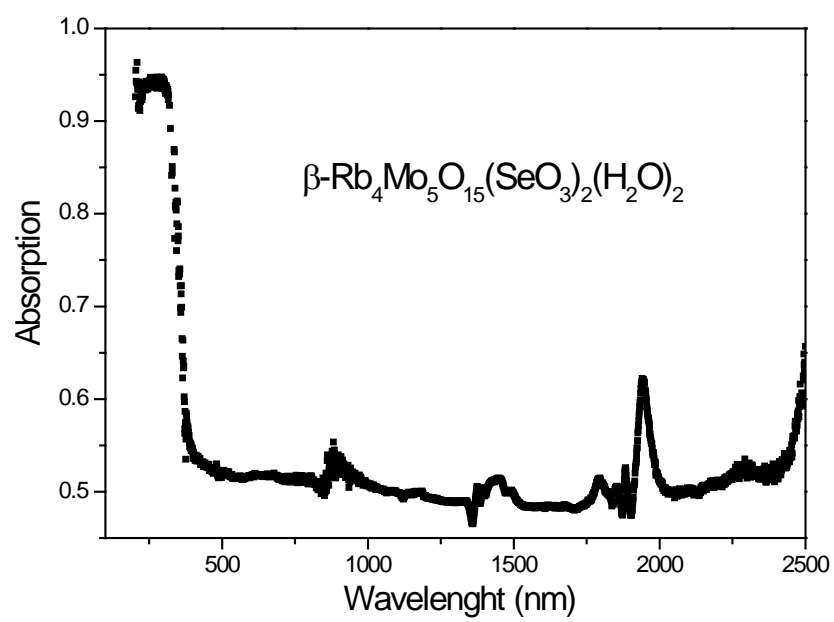
Figure S3. IR spectra for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **1**, $\alpha\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **2**, $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2(\text{H}_2\text{O})_2$ **4**.



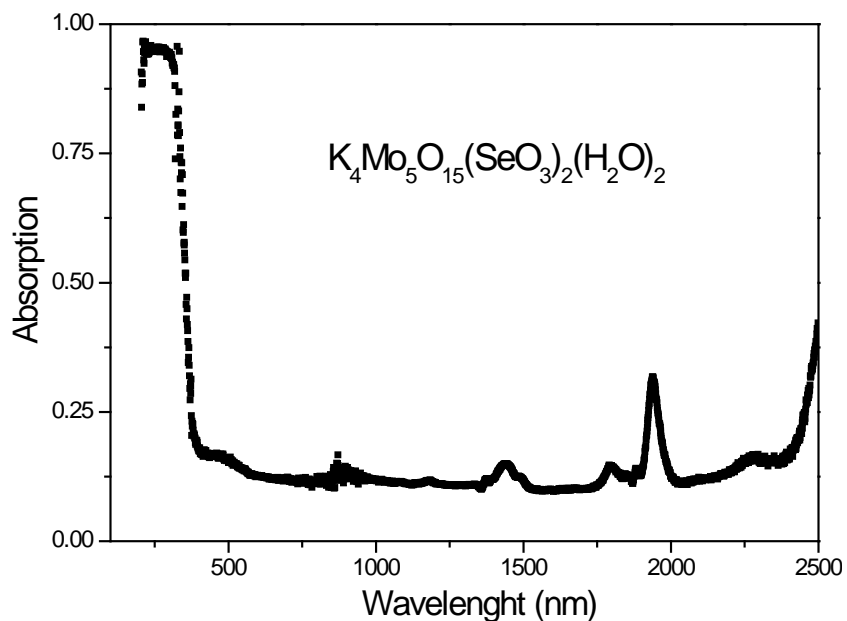
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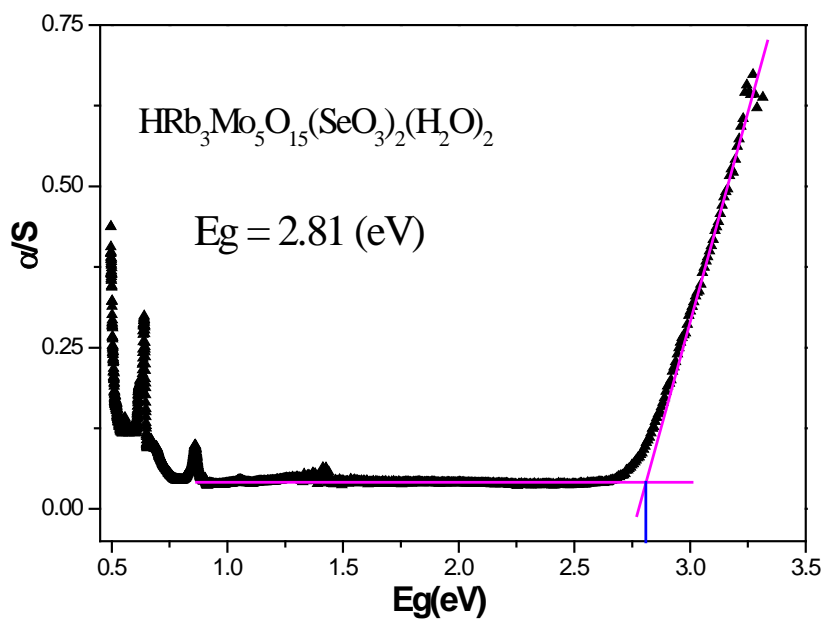


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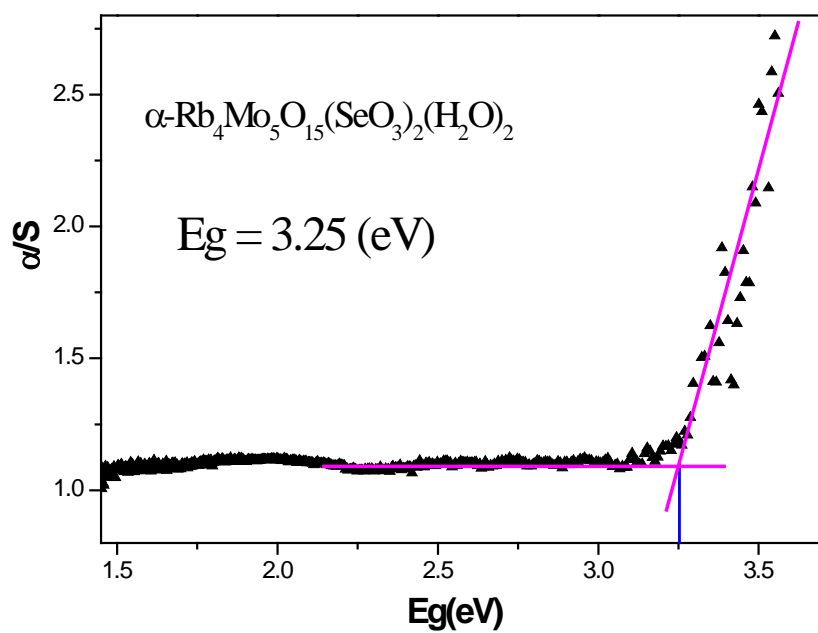


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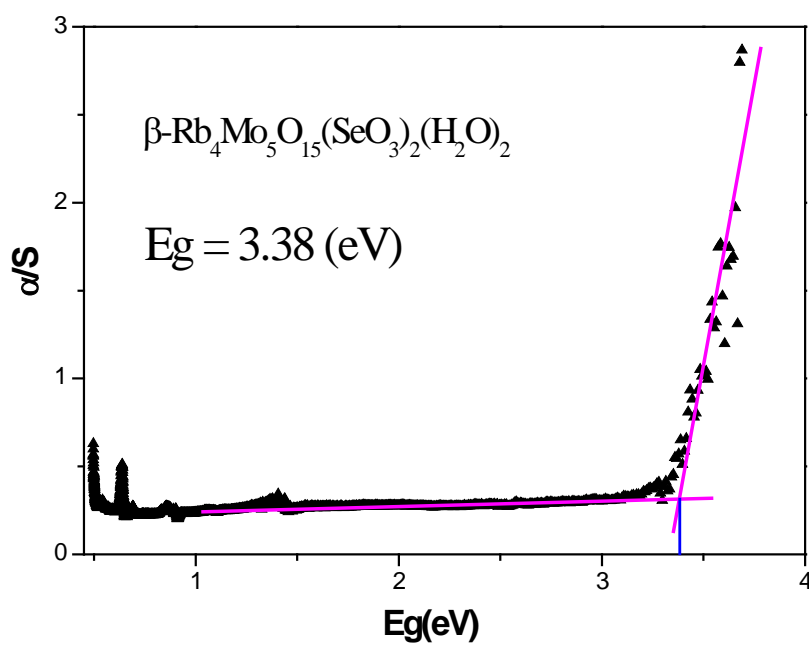
Figure S4. UV-Visible absorption spectra for $\text{HRb}_3(\text{Mo}_5\text{O}_{15})(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **1**, $\alpha\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **2**, $\beta\text{-Rb}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **3** and $\text{K}_4\text{Mo}_5\text{O}_{15}(\text{SeO}_3)_2 \cdot (\text{H}_2\text{O})_2$ **4**.



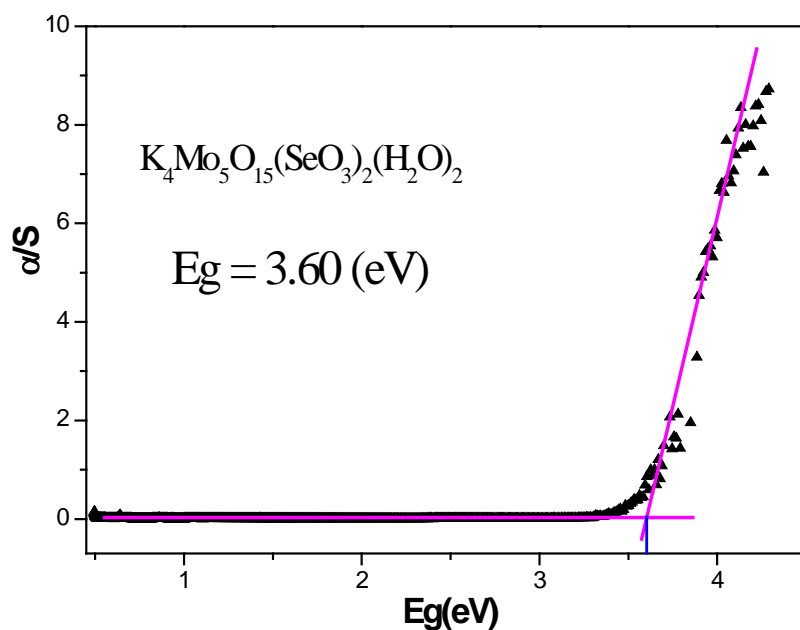
(a)



(b)



(c)



(d)

Figure S5. Optical diffuse reflectance spectra for $HRb_3(Mo_5O_{15})(SeO_3)_2(H_2O)_2$ **1**, $\alpha\text{-}Rb_4Mo_5O_{15}(SeO_3)_2 \cdot (H_2O)_2$ **2**, $\beta\text{-}Rb_4Mo_5O_{15}(SeO_3)_2(H_2O)_2$ **3** and $K_4Mo_5O_{15}(SeO_3)_2(H_2O)_2$ **4**.

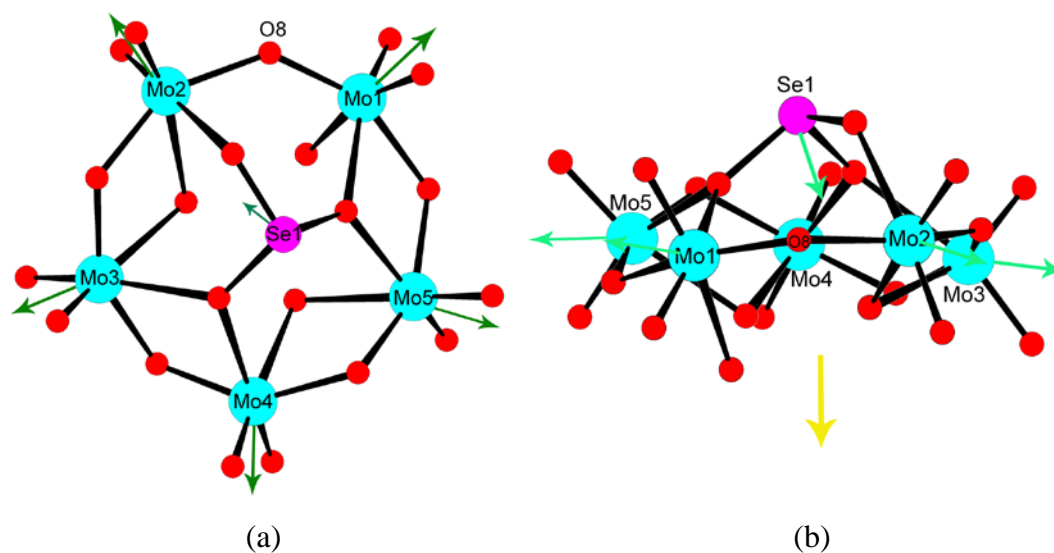


Figure S6. View of the structure of polyanion $[Mo_5O_{15}(SeO_3)]^{2-}$ with the macroscopic polarity indicated by small green arrows: viewed from above the Mo_5 ring (a) and along the C_2 axis in the plane of the Mo_5 ring (b). MoO_6 octahedra are shaded in blue, Rb, Se and O atoms are drawn as green, pink and red circles, respectively.