## Electronic Supplementary Information:

## Rb$_2$SeOCl$_4$·H$_2$O: A polar material among the alkali metal selenite halides with strong SHG response

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**Figure S1.** X-ray diffraction powder patterns for Rb$_2$SeOCl$_4$·H$_2$O: Calculated and experimental.

**Figure S2.** The EDX spectrum of Rb$_2$SeOCl$_4$·H$_2$O crystal

**Figure S3.** FTIR spectrum for Rb$_2$SeOCl$_4$·H$_2$O ( 4000 − 400 cm$^{-1}$ region)

**Figure S4.** The total and partial density of states (T/PDOS) of Rb$_2$SeOCl$_4$·H$_2$O

**Table S1.** Atomic coordinates and equivalent isotropic displacement parameters for Rb$_2$SeOCl$_4$·H$_2$O.

**Table S2.** Bond lengths(Å) for Rb$_2$SeOCl$_4$·H$_2$O

**Table S3.** Bond angles(°) for Rb$_2$SeOCl$_4$·H$_2$O

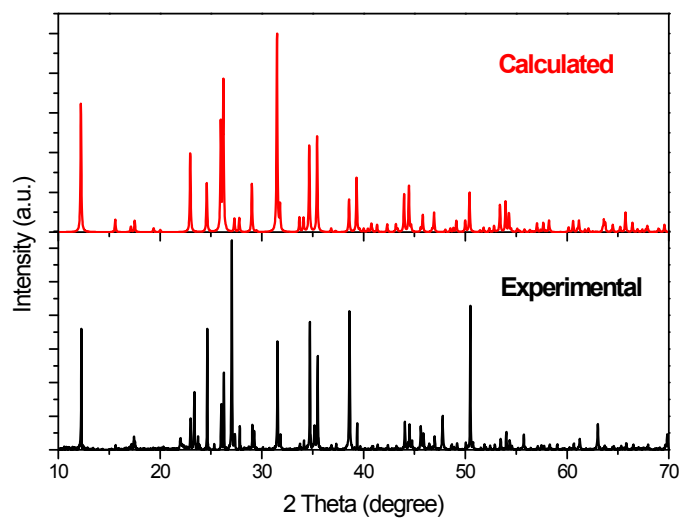**Table S4.** The calculated linear and nonlinear optical properties of Rb$_2$SeOCl$_4$·H$_2$O

**Figure S1.** X-ray diffraction powder patterns for $Rb_2SeOCl_4 \cdot H_2O$: Calculated and experimental.
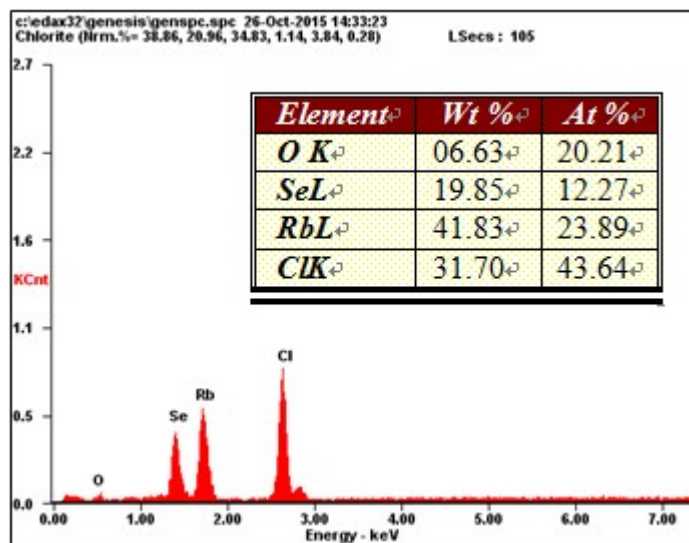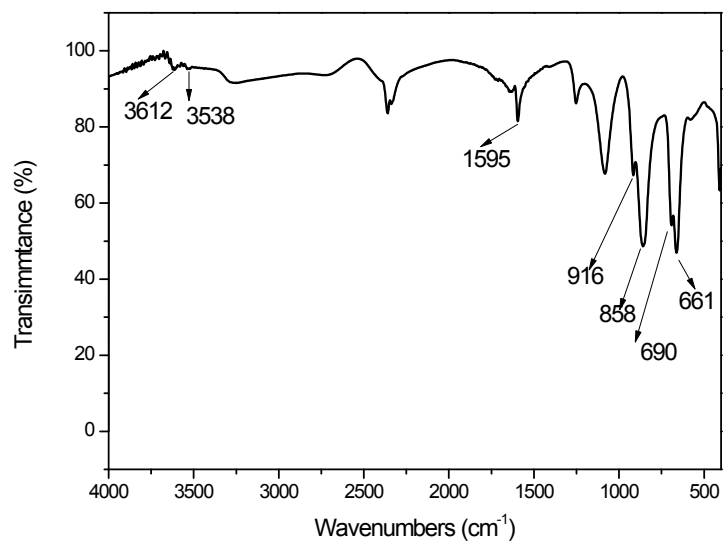


**Figure S2.** The EDX spectrum of $Rb_2SeOCl_4 \cdot H_2O$ crystal

**Figure S3.** FTIR spectrum for $Rb_2SeOCl_4 \cdot H_2O$ ($4000 - 400$ cm$^{-1}$ region)



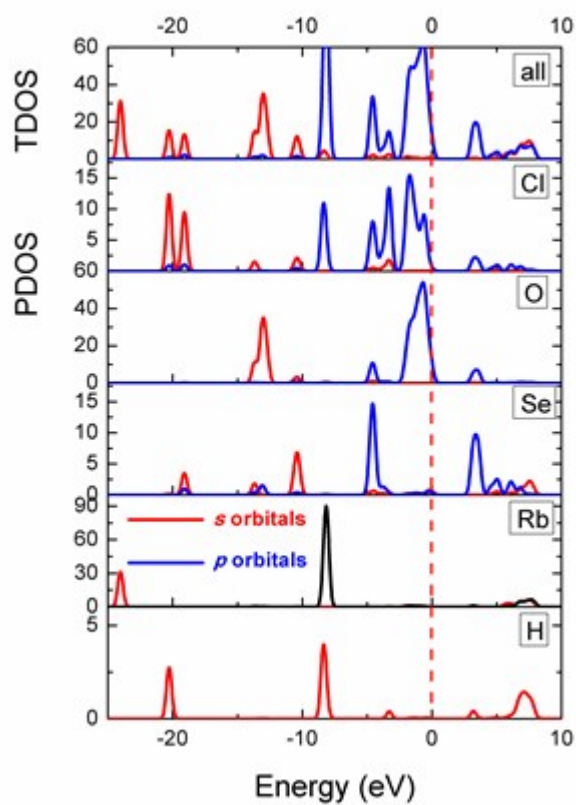**Figure S4** The total and partial density of states (T/PDOS) of $Rb_2SeOCl_4 \cdot H_2O$

**Table S1.** Atomic coordinates and equivalent isotropic displacement parameters for

$Rb_2SeOCl_4 \cdot H_2O$

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 10000 | 7662(2) | 7504(4) | 32(1) |
| Cl(2) | 10000 | 7517(2) | 3331(4) | 33(1) |
| Cl(3) | 7613(2) | 9967(2) | 2893(2) | 34(1) |
| O(1) | 5000 | 9615(7) | 5396(12) | 55(2) |
| O(2) | 5000 | 5387(7) | 5861(7) | 32(2) |
| Rb(1) | 7180(1) | 7582(1) | 5383(1) | 36(1) |
| Se(1) | 5000 | 5100(1) | 7606(2) | 21(1) |

[a]U(eq) is defined as one third of the trace of the othogonalized $U^{ij}$ tensor


**Table S2.** Bond lengths(Å) for $Rb_2SeOCl_4 \cdot H_2O$.

| Bond | Bond distances | Bond | Bond distances |
|---|---|---|---|
| Se(1)-Cl(1)#12 | 2.470(2) | Se(1)-O(2) | 1.624(7) |
| Se(1)-Cl(3)#3 | 2.483(2) | O(1)-H(1A) | 0.8500 |
| Se(1)-Cl(3)#13 | 2.483(2) | O(1)-H(1B) | 0.8500 |
| Se(1)-Cl(2)#3 | 2.502(3) | | |


**Table S3.** Bond angles(°) for $Rb_2SeOCl_4 \cdot H_2O$.

| Bond | Angles | Bond | Angles |
|---|---|---|---|
| O(2)-Se(1)-Cl(1)#12 | 98.2(3) | O(2)-Se(1)-Cl(2)#3 | 95.1(3) |
| O(2)-Se(1)-Cl(3)#3 | 96.25(6) | Cl(1)#12-Se(1)-Cl(2)#3 | 166.79(16) |
| Cl(1)#12-Se(1)-Cl(3)#3 | 88.67(5) | Cl(3)#3-Se(1)-Cl(2)#3 | 89.90(5) |
| O(2)-Se(1)-Cl(3)#13 | 96.25(6) | Cl(3)#13-Se(1)-Cl(2)#3 | 89.90(5) |
| Cl(1)#12-Se(1)-Cl(3)#13 | 88.67(5) | H(1A)-O(1)-H(1B) | 110.2 |
| Cl(3)#3-Se(1)-Cl(3)#13 | 167.46(12) | | |


**Table S4.** The calculated linear and nonlinear optical properties of $Rb_2SeOCl_4 \cdot H_2O$

| | Cal. band gap (eV) | Cal. SHG $d_{ij}$ (pm/V) |
|---|---|---|
| $Rb_2SeOCl_4 \cdot H_2O$ | 3.14 | $d_{15} = d_{24} = 9.63$ $d_{33} = -4.67$ |

[#]$d_{36}$(KDP)=0.39 pm/V; $<d_{eff}>$(KDP)=0.33 pm/V