# *Supporting Information*

# First Investigation of Europium Silicate Melilite for Second-order Nonlinear Optical Application: Experimental and Theoretical Studies

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**Table S1.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($U_{eq}$[a], $Å^2 \times 10^3$) for **1**.

| atom | *x* | *y* | *z* | $U_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Eu(1) | 6649.5(5) | 1649.5(5) | 5084.2(11) | 9.9(3) |
| Mg(1) | 10000 | 0 | 0 | 9.1(10) |
| Si(1) | 8618(3) | 3618(3) | -540(7) | 7.7(6) |
| O(1) | 5000 | 0 | 1570(20) | 10(2) |
| O(2) | 8608(8) | 3608(8) | 2547(19) | 12.2(17) |
| O(3) | 9209(8) | 1902(9) | -1951(12) | 12.0(13) |

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

**Table S2.** Important bond lengths (Å) for **1**.

| Bond | Dist./Å | Bond | Dist./Å |
|---|---|---|---|
| Eu(1)–O(1) | 2.610(8) | Mg(1)–O(3) | 1.938(7) |
| Eu(1)–O(2)#4 | 2.740(7) | Si(1)–O(1)#11 | 1.657(5) |
| Eu(1)–O(2) | 2.583(10) | Si(1)–O(2) | 1.596(11) |
| Eu(1)–O(3)#1 | 2.572(7) | Si(1)–O(3) | 1.630(7) |
| Eu(1)–O(3)#3 | 2.797(6) | | |

Symmetry transformations used to generate equivalent atoms: #1 +*x*, +*y*, 1+*z*; #2 +*y*, 1-*x*, -*z*; #3 1-*y*, -1+*x*, -*z*; #4 1-*y*, -1+*x*, 1-*z*. #5 +*y*,1-*x*,1-*z*; #6 1/2+*y*,-1/2+*x*,1+*z*; #7 -1/2+*x*,1/2-*y*,-*z*; #8 +*x*,+*y*,-1+*z*; #9 1+*y*,1-*x*,1-*z*; #10 2-*x*,-*y*,-1+*z*; #11 1+*y*,1-*x*,-*z*;

**Table S3.** Calculated directions and magnitudes of dipole moments for structural units in **1**.

| **Unit** | **Vector Analysis of Dipole Moments** | | | | |
|---|---|---|---|---|---|
| | ***x*** | ***y*** | ***z*** | **Magnitude (Debye)** | **esu·cm/Å$^3$(× 10$^4$)** |
| $EuO_8$ | 21.4292 | -8.4201 | -3.1783 | 23.2425 | 0.1394 |
| $MgO_4$ | -102.81427 | 50.6032 | 100.4658 | 152.3969 | 0.9139 |
| $SiO_4$ | -65.5268 | -65.5268 | 119.6869 | 151.3686 | 0.9077 |

**Table S4.** Calculated valence state of ions in **1** by bond valence model.

| Atom | BVS | Atom | BVS |
|---|---|---|---|
| Eu(1) | 1.98 | O1 | -2.40 |
| Mg(1) | 2.06 | O2 | -1.78 |
| Si(1) | 3.96 | O3 | -1.99 |

**Table S5.** The SHG intensities of silicates.

| Compound | SHG intensity | Compound | SHG intensity |
|---|---|---|---|
| $Sr_2ZnSi_2O_7$[1] | ~35 × $\alpha$-$SiO_2$ (1.75 × KDP) | $Li_2K_4[(TiO)Si_4O_{12}]$[2] | ~4.5 × KDP |
| $Sr_2MgSi_2O_7$[1] | ~5 × $\alpha$-$SiO_2$ (0.25 × KDP) | $Li_2Rb_4[(TiO)Si_4O_{12}]$[2] | ~4.5 × KDP |
| $Rb_2ZnSi_3O_8$[3] | ~2.5 × $\alpha$-$SiO_2$ (0.13 × KDP) | $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$[4] | ~1 × KDP |
| $Ba_2TiOSi_2O7$[5] | ~5.5 × KDP | $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$[4] | ~1 × KDP, |
| $Sr_2TiOSi_2O_7$[6] | ~8 × KDP | $Eu_2MgSi_2O_7$ | ~0.7 × KTP (10.5 × KDP) |
| $Cs_2B_4SiO_9$[7] | ~4.6 × KDP | | |

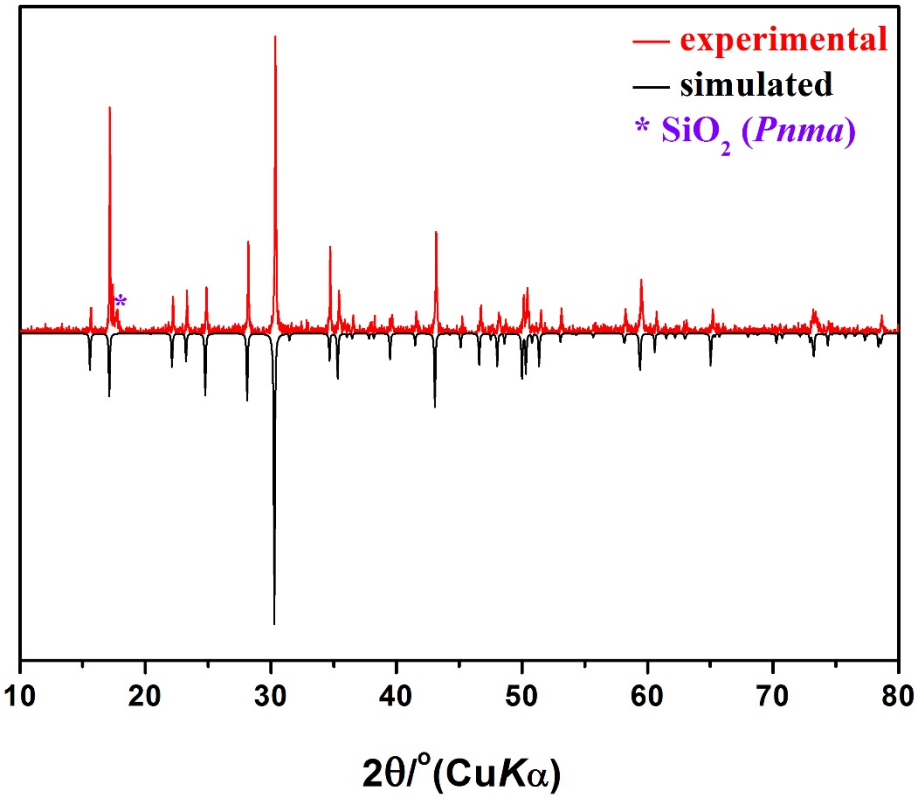



**Fig. S1** The X-ray powder diffraction pattern of **1**.

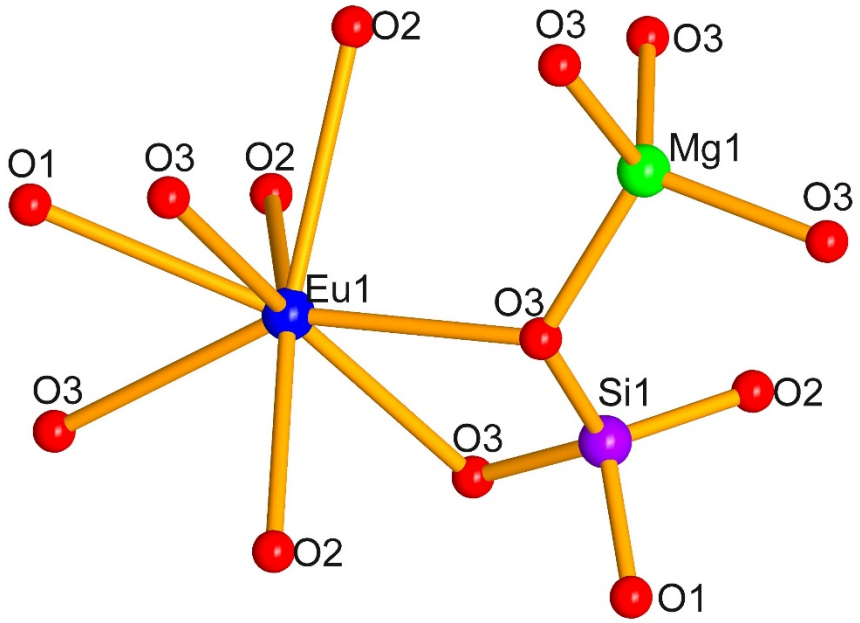
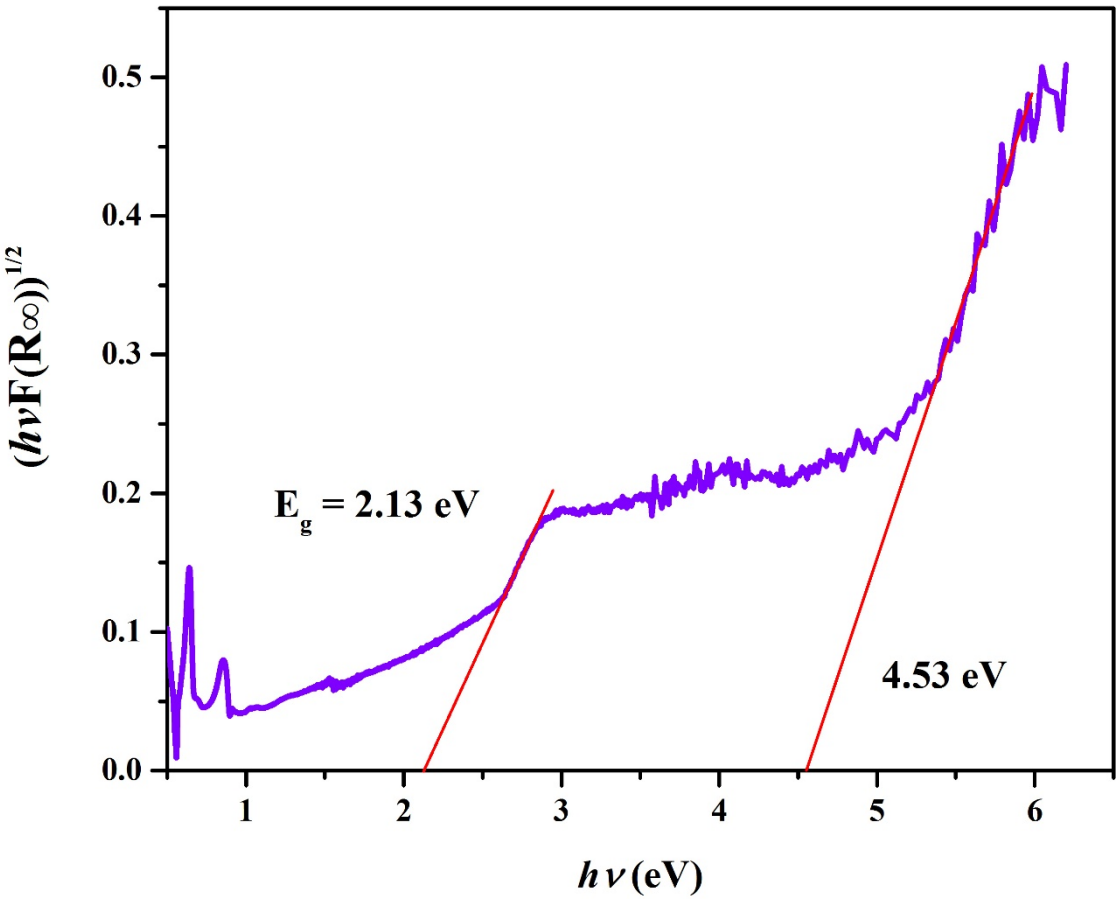
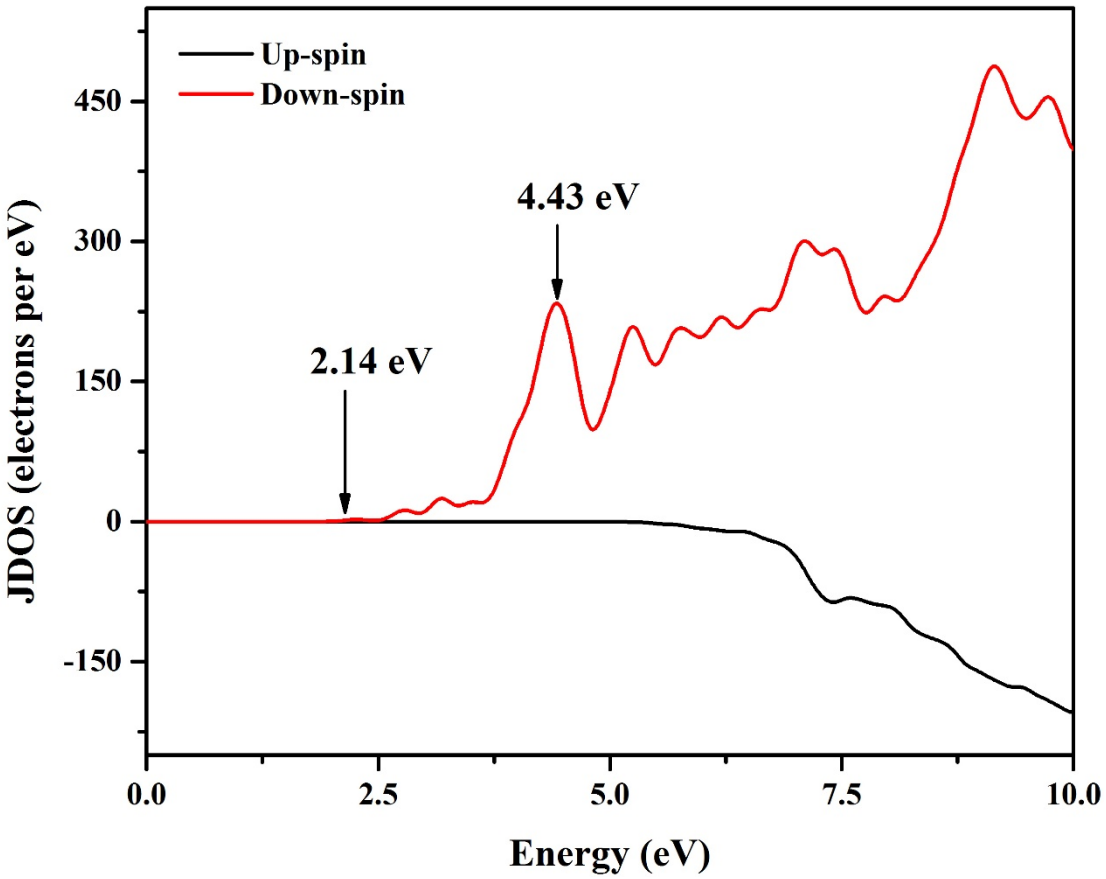



**Fig. S2** Coordination geometry of **1**.




(a)




(b)

**Fig. S3** (a) Tauc plot of **1**. (b) The joint density of states (JDOS) from DFT for **1**.

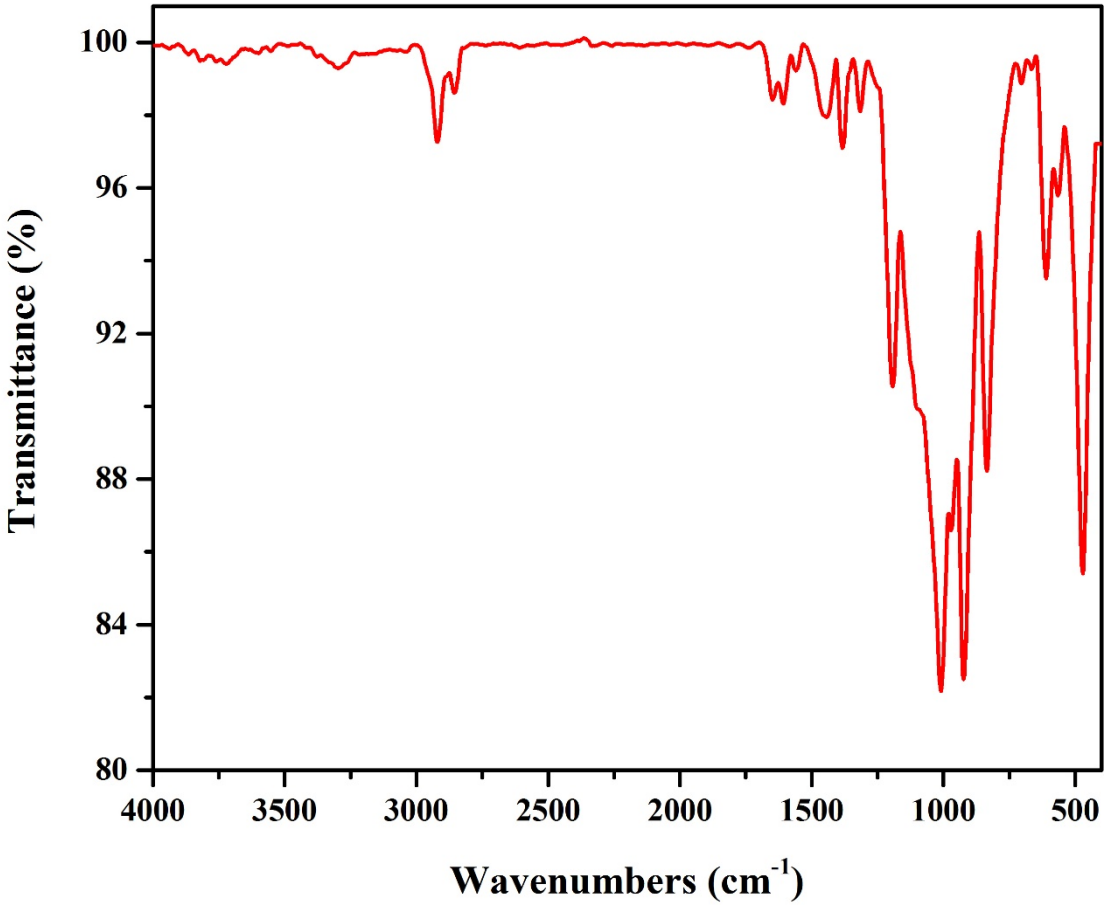
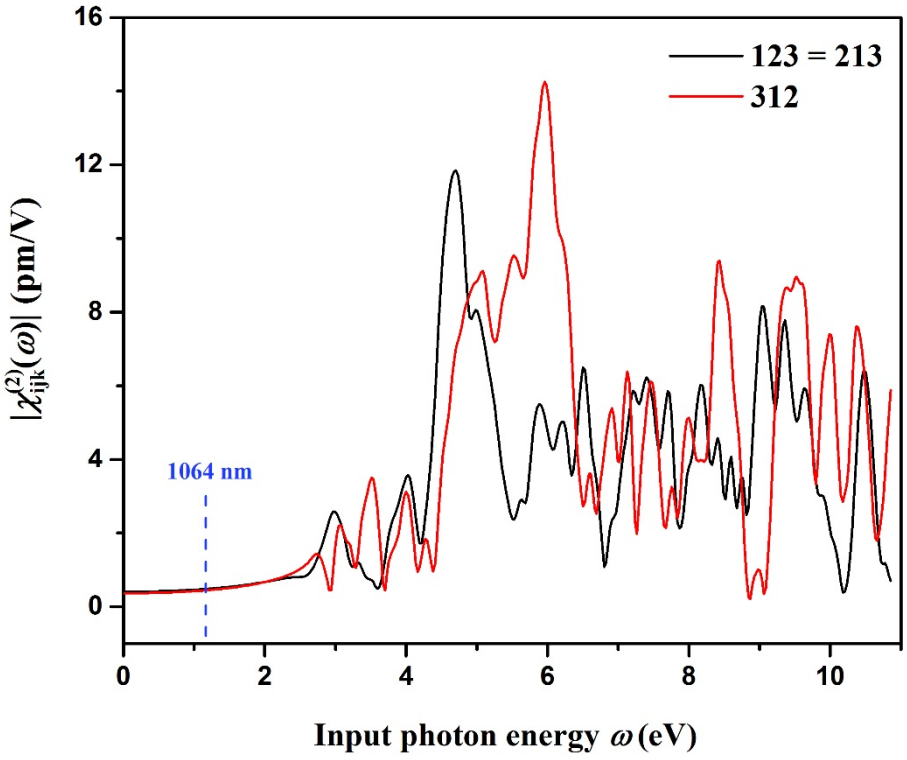
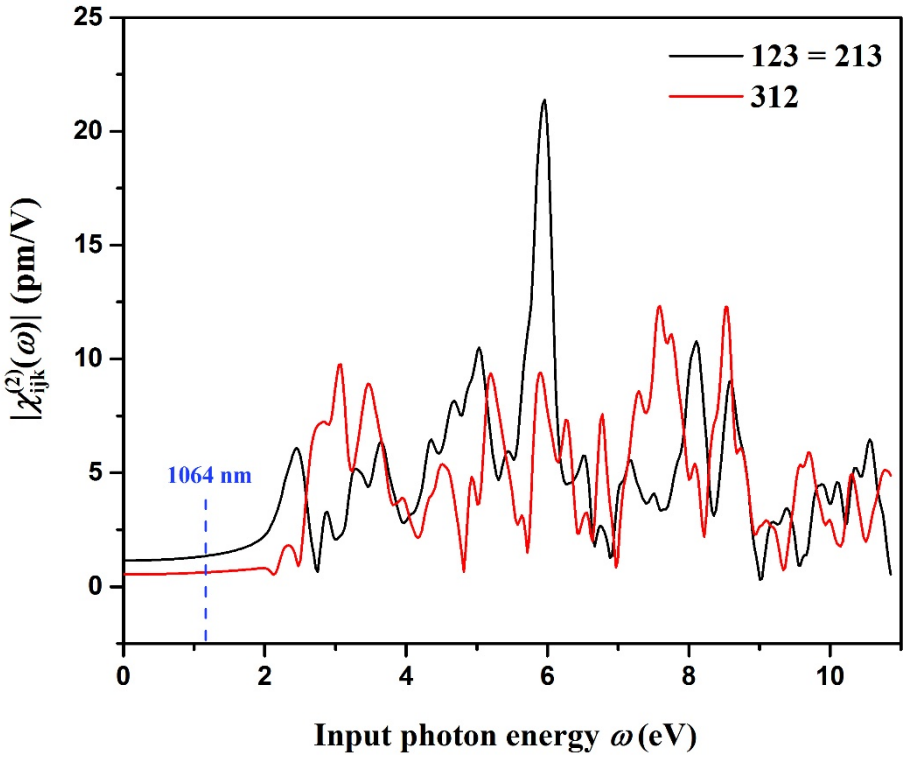


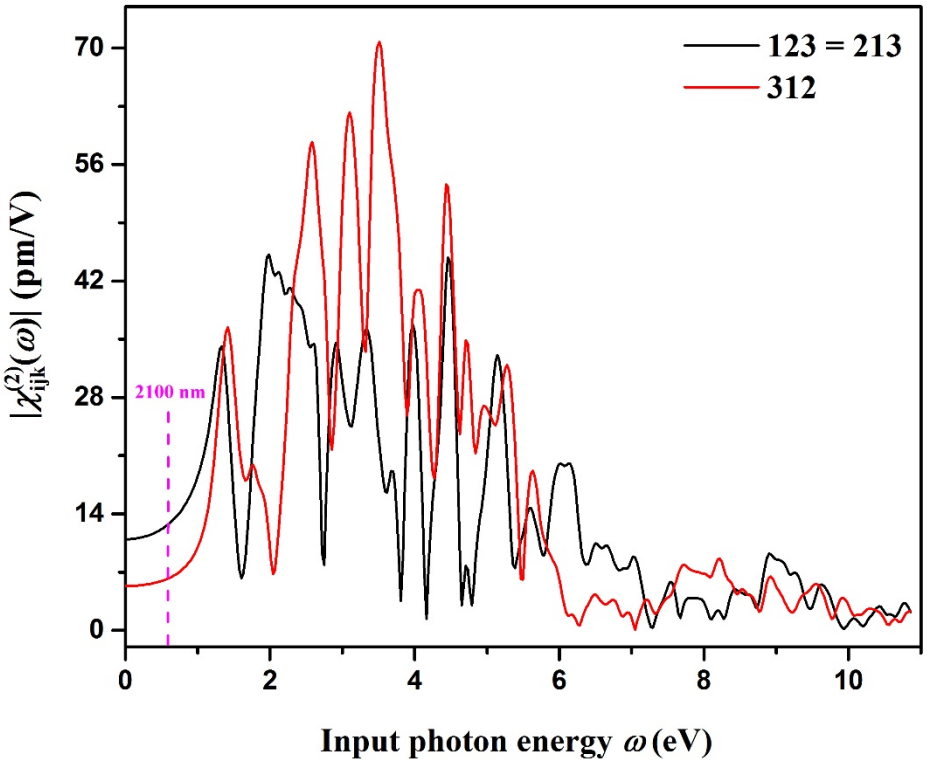

**Fig. S4** FT-IR of **1**.


123 = 213
312
1064 nm
$|\chi^{(2)}_{ijk}(\omega)|$ (pm/V)
Input photon energy $\omega$ (eV)

**(a)**


123 = 213
312
1064 nm
$|\chi^{(2)}_{ijk}(\omega)|$ (pm/V)
Input photon energy $\omega$ (eV)

**(b)**




**(c)**

**Fig. S5** Calculated absolute values of frequency dependence second-order susceptibilities $\left|\chi^{(2)}_{ijk}(\omega)\right|$ for $Sr_2MgSi_2O_7$ (a), $Sr_2MnSi_2O_7$ (b), and **1** (c).

## References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