Supporting Information

# Crystal Chemistry of Vanadium-Bearing Ellestadite Waste Forms

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**Table S1.** Lattice parameters and crystallographic data for hexagonal $Ca_{10}(SiO_4)_x(VO_4)_{6-2x}(SO_4)_xCl_2$, $0.19 \leq x \leq 3$.

| Single phase | | Miscibility gap | | | | | | Single phase | |
|---|---|---|---|---|---|---|---|---|---|
| *x* | | 0.90 (average) | | 1.47 (average) | | 2.14 (average) | | | |
| | 0.44 | 0.19 | 2.44 | 0.45 | 2.62 | 0.77 | 2.45 | 2.50 | 3.0 |
| Space group | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* | *P*6$_3$/*m* |
| Wt | 99.4% | 68.6% | 31.4% | 52.8% | 47.1% | 10.7% | 84.3% | 100% | 95.6% |
| *a* (Å) | 10.0541(4) | 10.1132(3) | 9.749(1) | 10.0583(7) | 9.6967(8) | 10.0177(4) | 9.7333(6) | 9.7245(4) | 9.6691(3) |
| *c* (Å) | 6.8223(3) | 6.8004(4) | 6.865(1) | 6.8256(9) | 6.8803(1) | 6.7744(4) | 6.8750(8) | 6.8722(4) | 6.8531(3) |
| *V* (Å$^3$) | 597.23(6) | 602.34(5) | 565.10(2) | 598.03(1) | 560.25(1) | 595.00(1) | 564.06(1) | 562.81(6) | 554.88(4)) |
| φ(deg) | $15.6_8$ | $13.4_6$ | $18.5_2$ | $15.4_8$ | $20.2_2$ | $16.0_3$ | $20.0_9$ | $19.9_2$ | $20.4_2$ |
| $R_{wp}$ | 0.076 | 0.072 | 0.072 | 0.078 | 0.078 | 0.075 | 0.075 | 0.079 | 0.052 |
| $R_p$ | 0.059 | 0.056 | 0.056 | 0.061 | 0.061 | 0.058 | 0.058 | 0.062 | 0.040 |
| $R_b$ | 0.023 | 0.026 | 0.014 | 0.024 | 0.016 | 0.014 | 0.023 | 0.028 | 0.032 |
| **Ca(1), 4*f* (1/3, 2/3, *z*)** | | | | | | | | | |
| *z* | 0.0039(9) | 0.001(1) | -0.009(3) | 0.0022(2) | 0.0023(2) | 0.0073(1) | 0.0002(1) | 0.006(1) | 0.0022(1) |
| *B* (Å$^2$) | 1.85(7) | 1.06(2) | 0.50(2) | 0.43(3) | 0.91(2) | 0.87(7) | 0.82(7) | 0.51(7) | 2.04(5) |
| **Ca(2), 6*h* (*x, y,* 1/4)** | | | | | | | | | |
| *x* | 0.2671(5) | 0.2688(9) | 0.251(2) | 0.2721(1) | 0.2499(1) | 0.2687(1) | 0.2549(1) | 0.2595(7) | 0.2600(7) |
| *y* | 0.0223(6) | 0.0201(9) | -0.016(2) | 0.0257(1) | 0.0122(2) | 0.0200(3) | 0.0054(1) | 0.0033(9) | 0.0004(8) |
| *B* (Å$^2$) | 1.85(7) | 1.06(2) | 0.50(2) | 0.43(3) | 0.91(2) | 0.87(7) | 0.82(7) | 0.51(7) | 2.04(5) |
| **Si/S, 6*h* (*x, y,* 1/4)** | | | | | | | | | |
| *x* | 0.4057(2) | 0.4060(2) | 0.4070(2) | 0.4055(2) | 0.4072(2) | 0.4046(1) | 0.4070(1) | 0.407(1) | 0.4030(4) |
| *y* | 0.3755(4) | 0.3756(3) | 0.3744(1) | 0.3760(2) | 0.3746(4) | 0.3733(1) | 0.3746(8) | 0.374(1) | 0.3728(4) |
| *B* (Å$^2$) | 0.80(4) | 1.39(2) | 0.86(2) | 1.39(2) | 1.38(4) | 0.87(7) | 1.16(3) | 0.82(6) | 2.04(5) |
| Occ. Si | 0.073 | 0.032 | 0.408 | 0.075 | 0.437 | 0.128 | 0.408 | 0.42 | 0.50 |
| S | 0.073 | 0.032 | 0.408 | 0.075 | 0.437 | 0.128 | 0.408 | 0.42 | 0.50 |
| V | 0.853 | 0.936 | 0.184 | 0.85 | 0.126 | 0.744 | 0.184 | 0.16 | |
| **O(1), 6*h* (*x, y,* 1/4)** | | | | | | | | | |
| *x* | 0.3491(2) | 0.3543(4) | 0.3436(7) | 0.3499(6) | 0.3299(6) | 0.3438(4) | 0.3338(5) | 0.3368(3) | 0.3361(3) |
| *y* | 0.5042(2) | 0.5090(4) | 0.4956(8) | 0.5060(6) | 0.4881(6) | 0.4960(3) | 0.4883(5) | 0.4885(3) | 0.4880(3) |
| *B* (Å$^2$) | 0.80(4) | 1.39(2) | 0.86(2) | 1.39(2) | 1.38(4) | 0.87(7) | 1.16(3) | 0.82(6) | 2.20(3) |
| **O(2), 6*h* (*x, y,* 1/4)** | | | | | | | | | |
| *x* | 0.5986(2) | 0.6008(4) | 0.5935(7) | 0.5998(6) | 0.5958(6) | 0.6005(8) | 0.5960(5) | 0.5929(3) | 0.5886(3) |
| *y* | 0.4648(4) | 0.4662(7) | 0.4659(1) | 0.4659(1) | 0.4761(1) | 0.4701(3) | 0.4674(8) | 0.4696(3) | 0.4672(5) |
| *B* (Å$^2$) | 0.80(4) | 1.39(2) | 0.86(2) | 1.39(2) | 1.38(4) | 0.87(7) | 1.16(3) | 0.82(6) | 2.20(3) |
| **O(3), 12*i* (*x, y, z*)** | | | | | | | | | |
| *x* | 0.3521(3) | 0.3530(4) | 0.3493(1) | 0.3508(8) | 0.3507(8) | 0.3521(3) | 0.3481(6) | 0.3487(4) | 0.3538(3) |
| *y* | 0.2611(2) | 0.2618(3) | 0.2750(1) | 0.2587(5) | 0.2675(5) | 0.2618(2) | 0.2650(5) | 0.2659(3) | 0.2665(3) |
| *z* | 0.0541(2) | 0.0527(4) | 0.0572(5) | 0.0563(6) | 0.0627(6) | 0.0053(2) | 0.0655(5) | 0.0661(3) | 0.0657(3) |
| *B* (Å$^2$) | 0.80(4) | 1.39(2) | 0.86(2) | 1.39(2) | 1.38(4) | 0.87(7) | 1.16(3) | 0.82(6) | 2.20(3) |

| **Cl *** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *x* | 0.017(7) | 0.011(6) | 0 | 0.019(7) | 0 | 0.011(8) | 0 | 0 | 0 |
| *y* | -0.020(7) | -0.029(4) | 0 | -0.030(6) | 0 | -0.023(9) | 0 | 0 | 0 |
| z | 0.3183(1) | 0.3223(1) | 0.358(4) | 0.287(5) | 0.353(2) | 0.404(4) | 0.327(4) | 0.381(2) | 0.425(1) |
| B ($Å^2$) | 1.85(7) | 1.06(2) | 1.06(2) | 0.43(3) | 0.91(2) | 0.87(7) | 0.82(7) | 0.51(7) | 2.04(5) |
| Occ | 0.144(2) | 0.154(3) | 0.50 | 0.137(5) | 0.50(4) | 0.146(2) | 0.50 | 0.488(9) | 0.416(2) |

$R_p = (\Sigma_i \mid y_i - y_{ci} \mid)/\Sigma_i yi$, $R_{wp} = [(\Sigma_i w \mid y_i - y_{ci} \mid^2)/\Sigma_i w \mid y_i^2]^{1/2}$; *Cl in V-rich phases at the site of 12*i* (*x, y, z*), while at 4*e* ( 0, 0, *z*) in (Si/S)-rich phases**.**

**Table S2.** Bond lengths for $Ca_{10}(SiO_4)_x(VO_4)_{6-2x}(SO_4)_xCl_2$.

| Composition *x* | 0.19 | 0.44 | 0.45 | 0.77 | 2.44 | 2.45 | 2.50 | 2.62 | 3.0 |
|---|---|---|---|---|---|---|---|---|---|
| Bond length (Å) | | | | | | | | | |
| Ca(1)-O(1) × 3 | 2.407(1) | 2.402(2) | 2.402(1) | 2.411(5) | 2.416(1) | 2.445(5) | 2.421(6) | 2.440(4) | 2.438(3) |
| Ca(1)-O(2) × 3 | 2.462(1) | 2.473(3) | 2.468(1) | 2.502(4) | 2.474(6) | 2.454(2) | 2.516(7) | 2.500(8) | 2.466(3) |
| < Ca(1)-O> | 2.434 | 2.437 | 2.435 | 2.456 | 2.445 | 2.450 | 2.468 | 2.47 | 2.452 |
| | | | | | | | | | |
| Ca(2)-O(1) | 3.407(7) | 3.318(2) | 3.389(3) | 3.224(2) | 2.827(2) | 2.836(8) | 2.866(9) | 2.746(1) | 2.893(4) |
| Ca(2)-O(2) | 2.327(1) | 2.345(3) | 2.294(1) | 2.274(6) | 2.387(2) | 2.340(8) | 2.241(8) | 2.301(9) | 2.283(4) |
| Ca(2)-O(3) × 2 | 2.330(5) | 2.354(2) | 2.374(9) | 2.320(1) | 2.223(1) | 2.315(4) | 2.331(4) | 2.289(4) | 2.582(3) |
| Ca(2)-O(3) × 2 | 2.534(7) | 2.495(2) | 2.451(1) | 2.511(8) | 2.837(2) | 2.640(9) | 2.572(8) | 2.706(5) | 2.358(3) |
| < Ca(2)-O> | 2.577 | 2.56 | 2.555 | 2.527 | 2.555 | 2.514 | 2.485 | 2.506 | 2.509 |
| | | | | | | | | | |
| B-O(1) | 1.673(5) | 1.653(3) | 1.660(7) | 1.621(5) | 1.581(9) | 1.586(9) | 1.554(3) | 1.609(7) | 1.544(5) |
| B-O(2) | 1.707(4) | 1.681(2) | 1.694(5) | 1.699(2) | 1.575(6) | 1.593(3) | 1.571(3) | 1.587(5) | 1.545(1) |
| B-O(3) | 1.671(2) | 1.667(1) | 1.671(4) | 1.644(3) | 1.571(5) | 1.569(6) | 1.562(2) | 1.573(4) | 1.545(2) |
| Average | 1.680 | 1.667 | 1.674 | 1.652 | 1.574 | 1.579 | 1.562 | 1.585 | 1.545 |

**Table S3.** Bond lengths and angles of $Ca_{10}(VO_4)_6Cl_2$.

| <Ca-O> (Å) | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) | average |
|---|---|---|---|---|---|---|---|
| Ca(1) | 2.310(1) | 2.347(5) | 2.320(2) | 2.414(4) | 2.443(1) | 2.502(1) | 2.389 |
| Ca(2) | 2.448(1) | 2.388(5) | 2.507(2) | 2.523(4) | 2.412(1) | 2.421(2) | 2.450 |
| | | | | | | | |
| <V-O> (Å) | | | | | | | |
| V(1) | O(1) | O(4) | O(7) | O(10) | | | |
| | 1.691(1) | 1.711(3) | 1.692(3) | 1.684(6) | | | 1.694 |
| V(2) | O(2) | O(5) | O(8) | O(11) | | | |
| | 1.695(3) | 1.682(2) | 1.711(1) | 1.709(8) | | | 1.699 |
| V(3) | O(3) | O(6) | O(9) | O(12) | | | |
| | 1.703(2) | 1.720(2) | 1.700(3) | 1.695(1) | | | 1.704 |
| | | | | | | | |
| ∠O-V-O (°) | | | | | | | |
| V(1) | O(1)-V(1)-O(4) | O(1)-V(1)-O(7) | O(1)-V(1)-O(10) | O(4)-V(1)-O(7) | O(4)-V(1)-O(10) | O(7)-V(1)-O(10) | |
| | 106.97(1) | 110.88(1) | 111.83(2) | 107.58(2) | 115.83(3) | 103.65(3) | 109.45 |
| V(2) | O(2)-V(2)-O(5) | O(2)-V(2)-O(8) | O(2)-V(2)-O(11) | O(5)-V(2)-O(8) | O(5)-V(2)-O(11) | O(8)-V(2)-O(11) | |
| | 108.18(7) | 116.33(4) | 119.21(2) | 101.67(5) | 105.30(6) | 104.31(3) | 109.16 |
| V(3) | O(1)-V(1)-O(4) | O(1)-V(1)-O(7) | O(1)-V(1)-O(10) | O(4)-V(1)-O(7) | O(4)-V(1)-O(10) | O(7)-V(1)-O(10) | |
| | 108.91(5) | 113.28(3) | 118.59(3) | 108.21(8) | 101.01(2) | 105.80(4) | 109.30 |

**Table S4**. Variation in the metaprism twist angle of calcium apatite as a function of average crystal radius.

| Composition | Average crystal radius (Å) | Twist angle φ (°) | Reference |
|---|---|---|---|
| $Ca_{10}(PO_4)_6F_2$ | 1.143 | 23.3 | [51] |
| $Ca_{10}(PO_4)_6(OH)_2$ | 1.146 | 23.2 | [52] |
| $Ca_{9.82}(SiO_4)_3(SO_4)_3Cl_{1.64}$ | 1.158 | 20.4 | this study |
| $Ca_{10}(PO_4)_6Cl_2$ | 1.166 | 19.1 | [52] |
| $Ca_{10}(CrO_4)_6(OH)_2$ | 1.171 | 17.8 | [53] |
| $Ca_{10}(PO_4)_6Br_2$ | 1.173 | 16.3 | [52] |
| $Ca_{10}(AsO_4)_6Cl_2$ | 1.189 | 13.0 | [54] |
| $Ca_{10}(VO_4)_6Cl_2$ | 1.192 | 11.6* | this study |
| $Ca_4Pb_6(AsO_4)_6Cl_2$ | 1.214 | 5.2 | [55] |

* The twist angle of $Ca_{10}(VO_4)_6Cl_2$ is the average value of three twist angles in a triclinic *P*-1 structure.

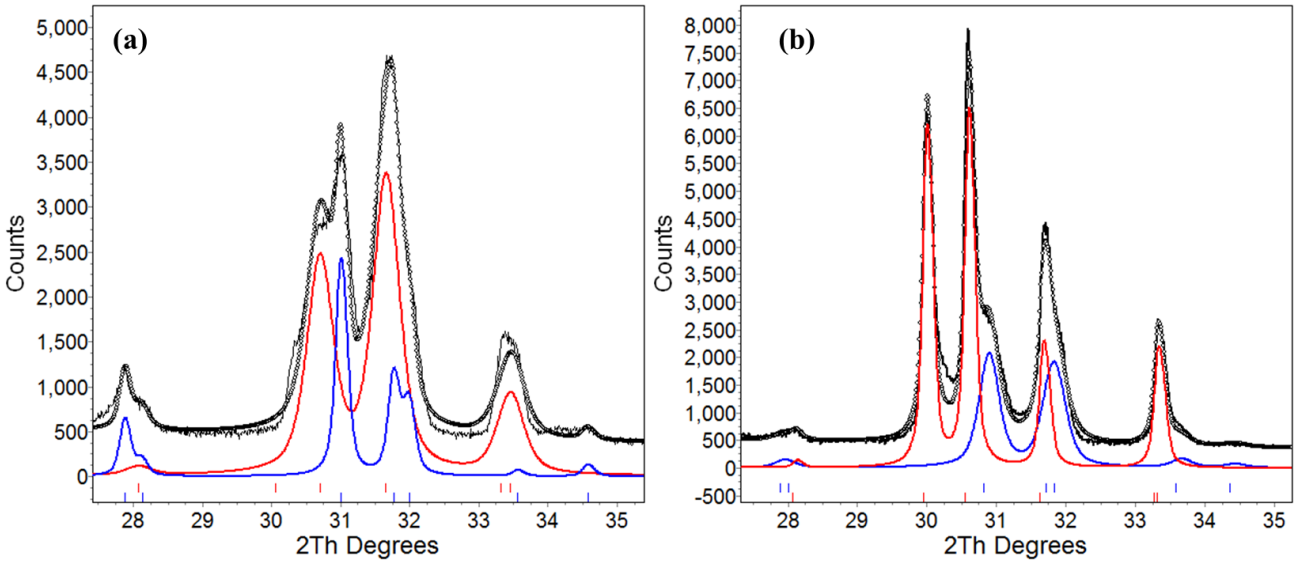


**Figure S1.** Rietveld fit between calculated (black dot) and experimental (black line) diffraction profiles for $Ca_{10}(SiO_4)_x(VO_4)_{6-2x}(SO_4)_xCl_2$, with (a) nominal $x = 1.5$ and (b) $x = 1.0$. At these compositions immiscibility is reflected by co-existing ellestadite phase pairs. The contributions of V-rich phase (red line) and (Si/S)-rich phase (blue line) are shown.

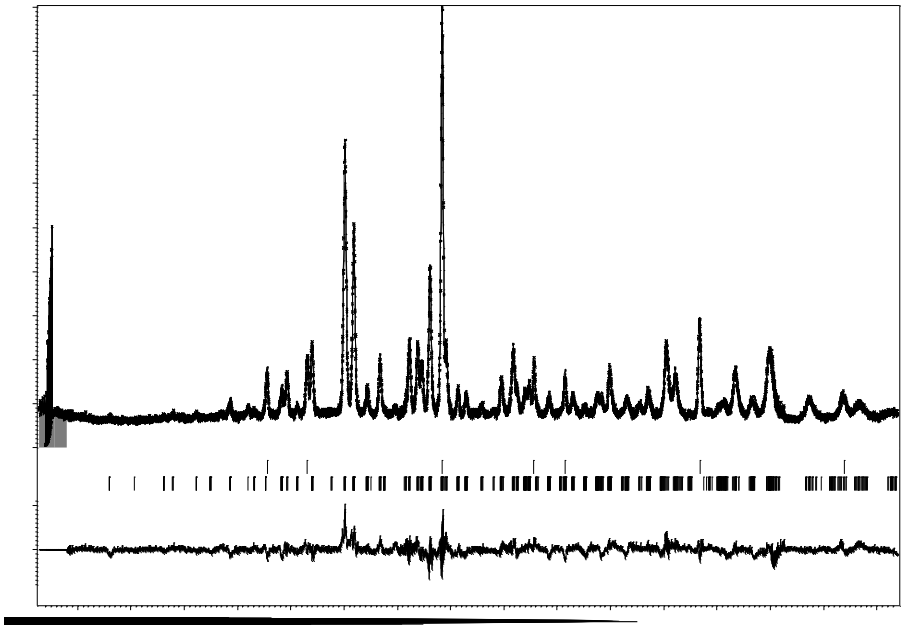

**Figure S2.** Neutron diffraction Rietveld profiles of $Ca_{10}(VO_4)_6Cl_2$. The calculated weight percentage of internal standard $CaF_2$ and $Ca_{10}(VO_4)_6Cl_2$ are 20.09(1)% and 79.91(1)% respectively. The differences between observed and calculated profile is shown.

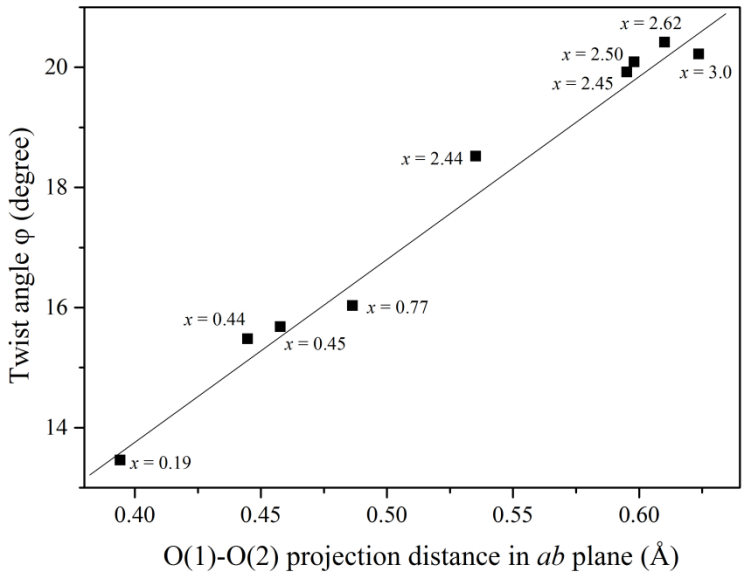


**Figure S3.** The relationship between metaprism twist angle φ of $Ca_{10}(SiO_4)_x(VO_4)_{6-2x}(SO_4)_xCl_2$ and the O(1)-O(2) projection distance in *ab* plane.

**Calulation of metaprism twist angle (φ)**

Metaprism twist angle is calculated by

$$\varphi = \arccos\left(\frac{{d_1}^2 + {d_2}^2 - {d_3}^2}{2 \times d_1 \times d_2}\right)$$

where $d_1$, $d_2$ and $d_3$ is the distance between the projections of Ca(1) and O(1), Ca(1) and O(2), and O(1) and O(2) in *ab* plane (Fig. S2). They are calculated from the cell parameters and fractional coordinates of Ca(1), O(1) and O(2) with the expression

$d_1^2 = (a\, x_{O1}\cos30° - a\, x_{Ca1}\cos30°)^2 + [(b\, y_{O1} - a\, x_{O1}\sin30°) - (b\, y_{Ca1} - a\, x_{Ca1}\sin30°)]^2$,

$d_2^2 = (a\, x_{O2}\cos30° - a\, x_{Ca1}\cos30°)^2 + [(b\, y_{O2} - a\, x_{O2}\sin30°) - (b\, y_{Ca1} - a\, x_{Ca1}\sin30°)]^2$,

$d_3^2 = (a\, x_{O1}\cos30° - a\, x_{O2}\cos30°)^2 + [(b\, y_{O1} - a\, x_{O1}\sin30°) - (b\, y_{O2} - a\, x_{O2}\sin30°)]^2$.

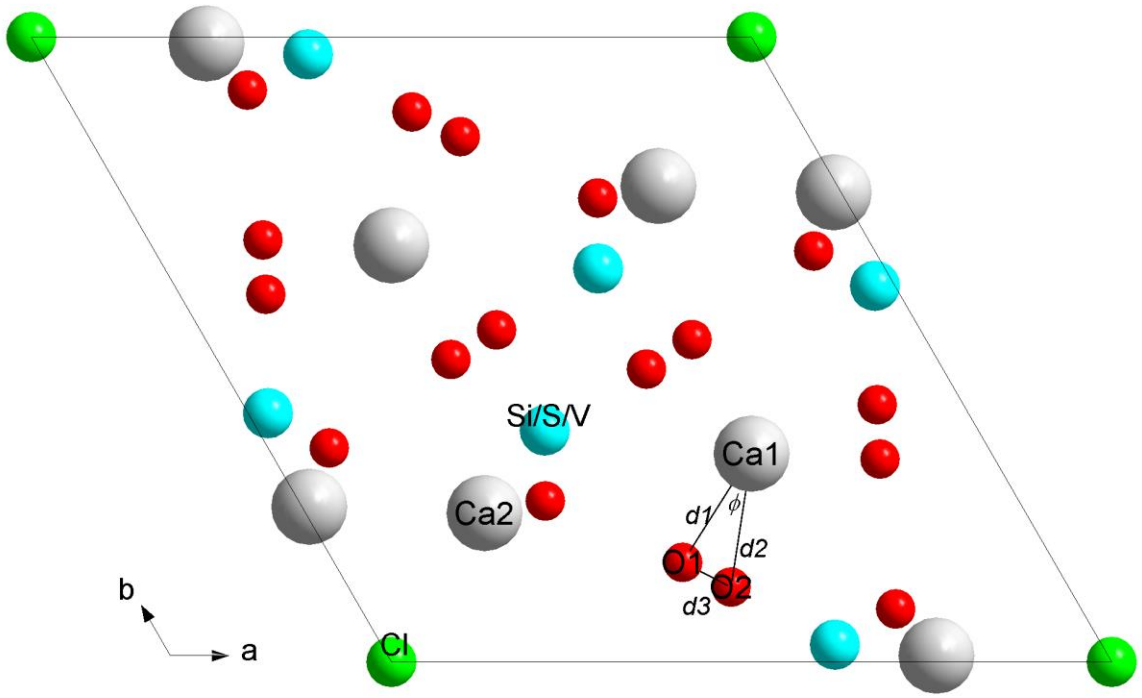


**Figure S4.** The projection of ellestadite unit cell in *ab* plane.