CHEM 548: MATERIALS CHEMISTRY

LECTURE 7: IMPORTANT TERNARY AND QUATERNARY STRUCTURES

Wed 09/16/2026

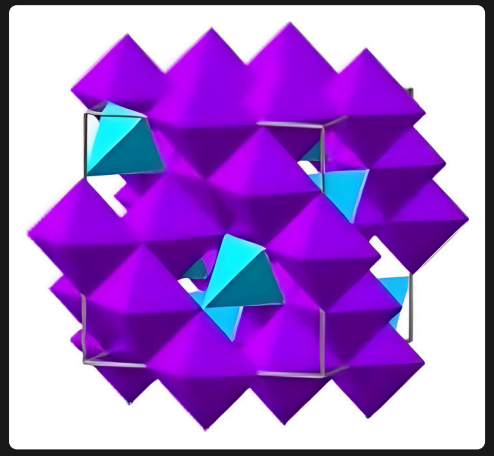
Spinel, garnet, perovskite, and Goldschmidt tolerance factors

Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry* Ch. 1 §1.5

LEARNING OBJECTIVES

Spinel, garnet, perovskite	recognize the structural features of the three lattices
Site preferences	how tetrahedral versus octahedral cation preferences shape these structures
Functional properties	magnetism, lasers, ferroelectricity, piezoelectricity
Parsimony and coordination	apply Pauling's rule of parsimony and coordination-number analysis to complex solids
Tolerance factor	predict perovskite stability and distortions

SPINEL ($MgAl_2O_4$)



Magnetite Fe_3O_4 = $Fe^{2+}Fe^{3+}{}_2O_4$

AB_2O_4 with A and B both iron; the oldest technologically used magnetic material, in compasses over 2000 years ago

Site occupation

Mg on tetrahedral sites, Al on octahedral sites

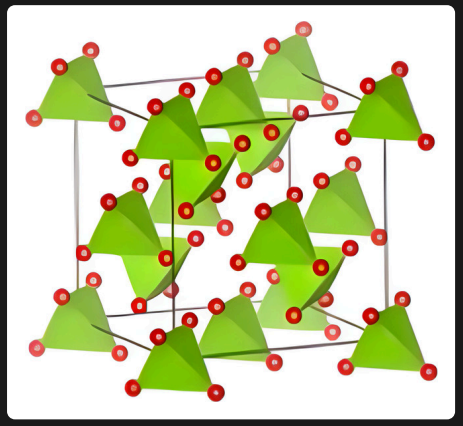


Compass (circa 4th century BC)

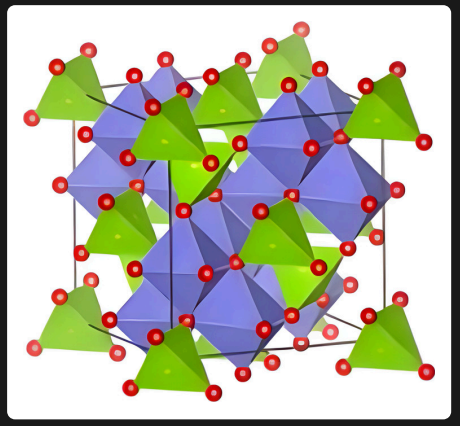
Tetrahedron	Octahedron	Example
1	3, 4	$LiMn_2O_4$ (a = 8.245 Å)
2	3, 3	$ZnFe_2O_4$ (a = 8.442 Å)
2	4, 2	Fe_2TiO_4 (a = 8.521 Å)
3	2, 3	$Fe_3O_4 = Fe^{2+}Fe^{3+}{}_2O_4$ (a = 8.394 Å)
4	2, 2	Ni_2SiO_4 (a = 8.045 Å)
5	1, 2	$LiZnNbO_4$ (a = 6.082, c = 8.403 Å)
6	1, 1	Na_2WO_4 (a = 9.108 Å)

Per *Solid State Materials Chemistry*, Table 1.7, §1.5.1.

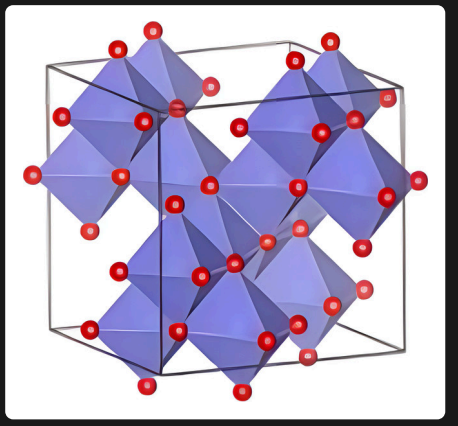
SPINEL STRUCTURE



MgO_4 tetrahedra not connected



ccp array of O; Al in 1/2 octahedral holes; Mg in 1/8 tetrahedral holes

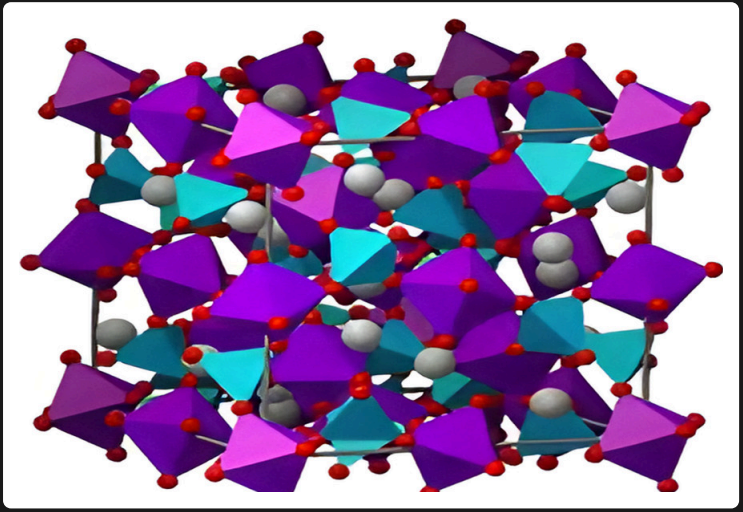


AlO_6 octahedra share edges

$$A^{[4]}B_2^{[6]}O_4^{[1,3]}$$

Normal spinel (e.g. $MgAl_2O_4$)	A tetrahedral (Mg), B octahedral (Al)
Inverse spinel (e.g. $TiFe_2O_4$)	B tetrahedral (Fe); B and A randomly octahedral (Fe, Ti)

GARNET (E.G. $Mg_3Al_2Si_3O_{12}$)

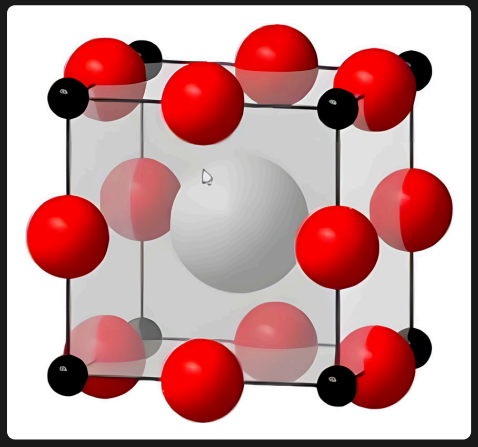


Space group $Ia\bar{3}d$, a = 11.459 Å

Atom	Site	Symmetry	x	y	z
Al	16a	$\bar{3}$	0	0	0
Mg	24c	222	1/8	0	1/4
Si	24d	$\bar{4}$	3/8	0	1/4
O	96h	1	0.034	0.050	0.654

$$Mg_3^{[8]}Al_2^{[6]}Si_3^{[4]}O_{12}^{[2,1,1]}$$

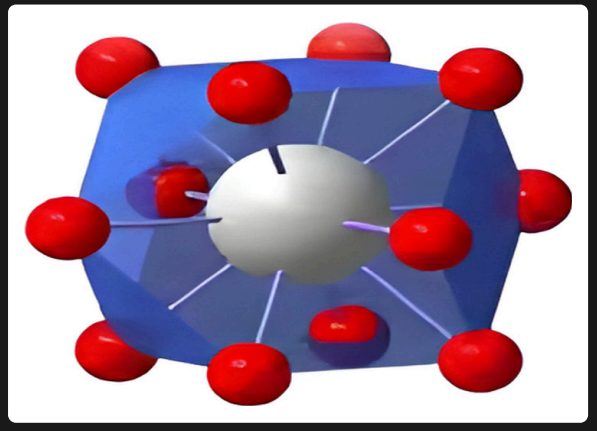
PEROVSKITES



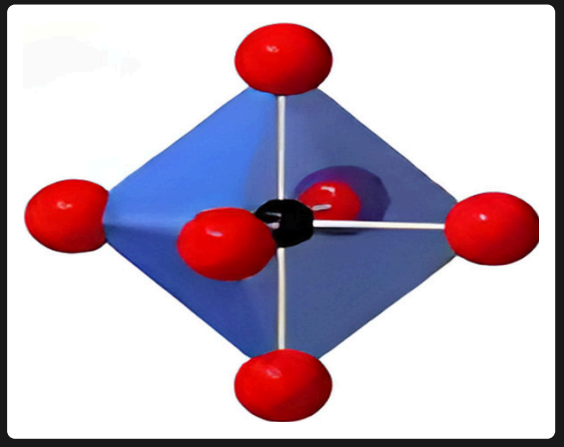
Space group $Pm\bar{3}m$, a = 4.0 Å

Atom	Site	Symmetry	x	y	z
Sr	1b	$m\bar{3}m$	1/2	1/2	1/2
Ti	1a	$m\bar{3}m$	0	0	0
O	3d	4/mmm	1/2	0	0

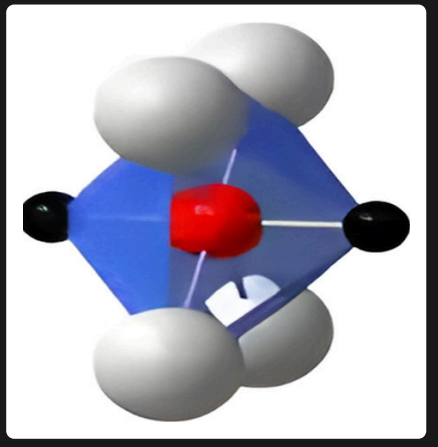
$$Sr^{[12]}Ti^{[6]}O_3^{[4,2]}$$



A-site: cubo-octahedron

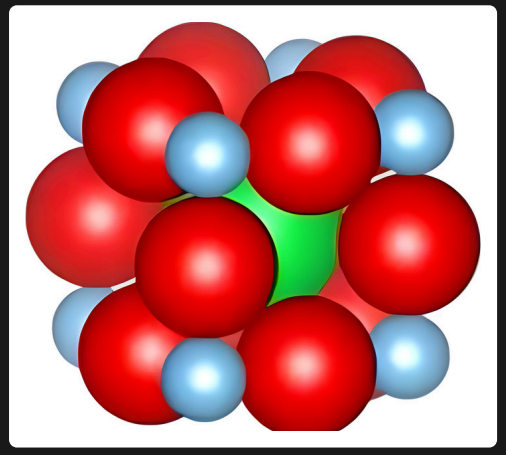


B-site: octahedron

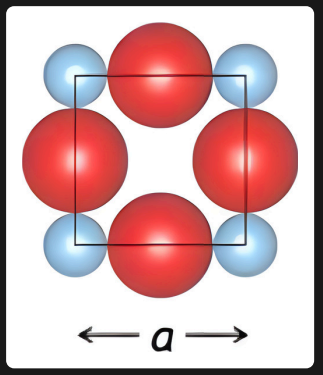


Anion

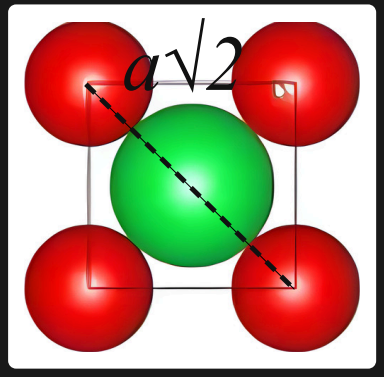
TOLERANCE FACTOR



● Sr ● Ti ● O



Cell face: Ti at the corners, O on the edges



Cell centre: Sr in the middle, O at the corners

for any ABO_3: Sr is the A cation, Ti the B cation

$$t = \frac{r_A + r_O}{\sqrt{2}\,(r_B + r_O)}$$

$t > 1$	$t = 1$	$t < 1$
A too big	perfect fit	A too small

Per *Solid State Materials Chemistry*, Ch. 1 §1.5.

SIZE MISMATCH AND ABO_3 COMPOUNDS

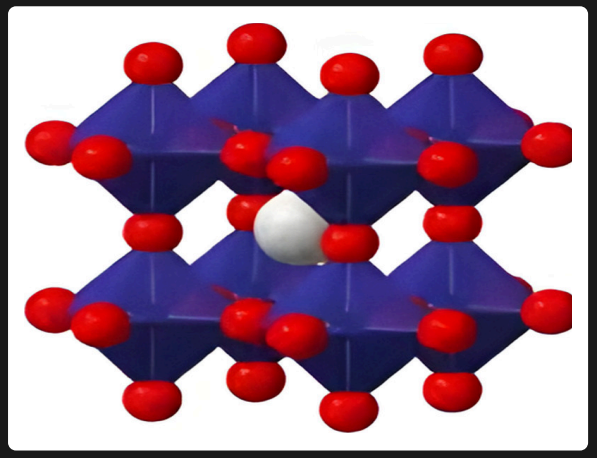
Cell edge each cation would prefer, and their ratio

Compound	a (Å) A-cation	a (Å) B-cation	Tolerance factor t
$BaMnO_3$	4.17	3.81	4.17/3.81 = 1.09
$BaTiO_3$	4.17	3.93	1.06
$SrTiO_3$	3.93	3.93	1.00
$CaMnO_3$	3.72	3.81	0.976
$CaTiO_3$	3.72	3.93	0.946
$MgTiO_3$	3.33	3.93	0.847

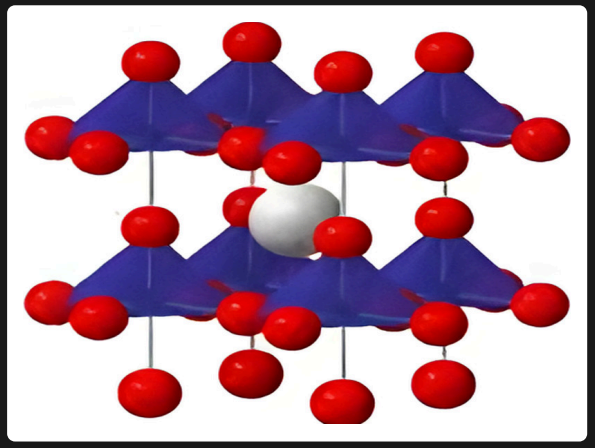
Not perovskite

Distorted perovskite

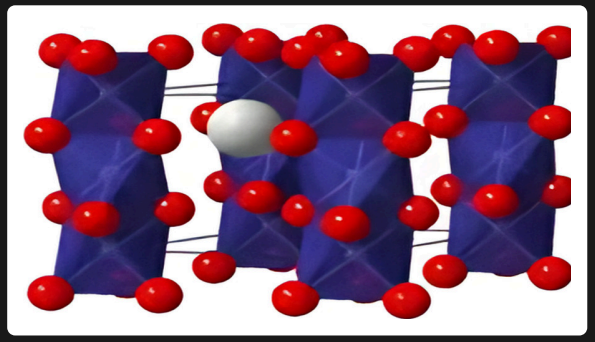
$ATiO_3$ STRUCTURES ($t > 1$)



$SrTiO_3$
t = 1.00
Cubic perovskite



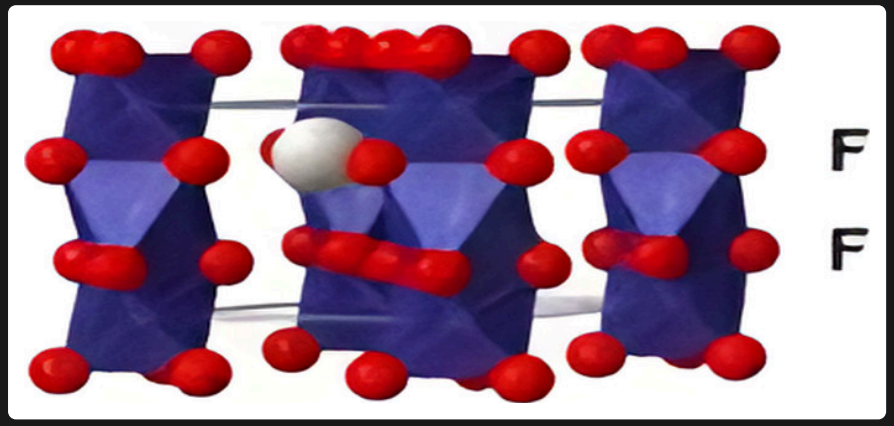
$BaTiO_3$
t = 1.06
Distorted perovskite



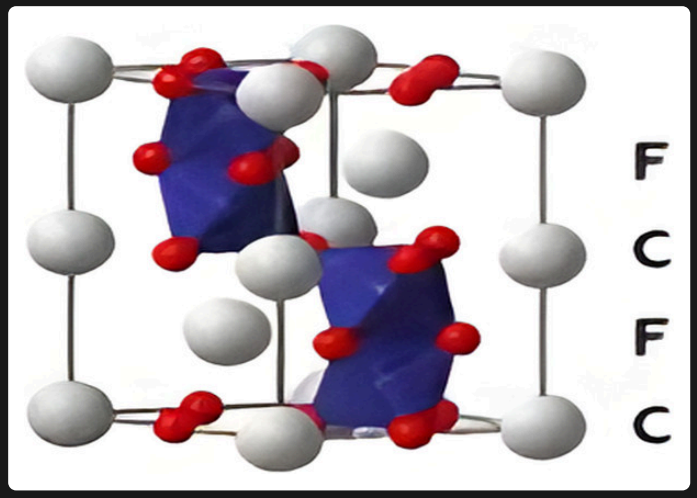
$BaMnO_3$
t = 1.09
2H “hexagonal” perovskite

As the tolerance factor rises above 1.00 the connectivity of the octahedral corner sharing network starts to break down, first subtly and then more dramatically.

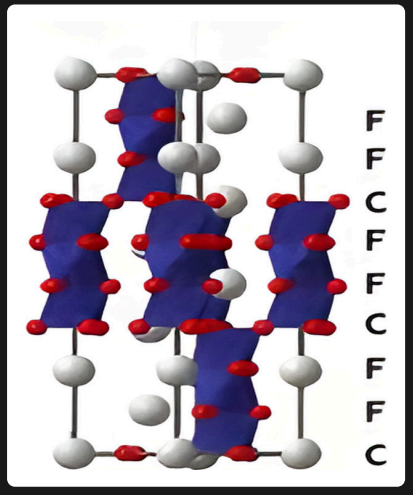
“HEXAGONAL/RHOMBOHEDRAL PEROVSKITES”



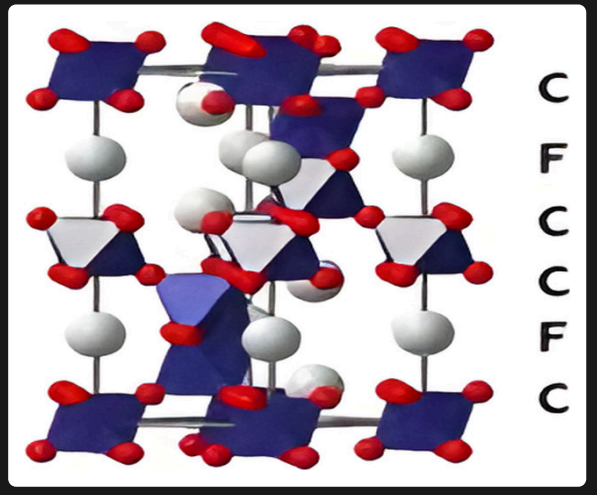
2H ($BaMnO_3$)



4H (HP-$BaRuO_3$)

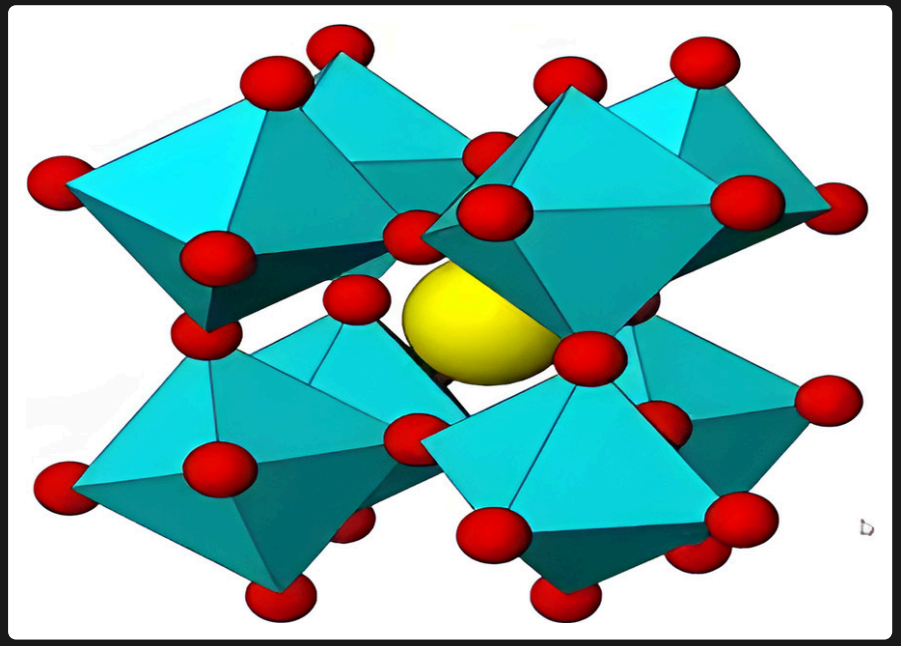


9R ($BaRuO_3$)



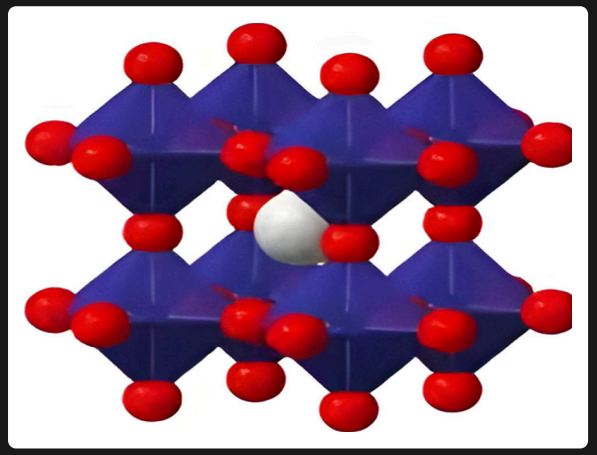
6H ($BaTiO_3$)

CRYSTAL STRUCTURE - $CaTiO_3$

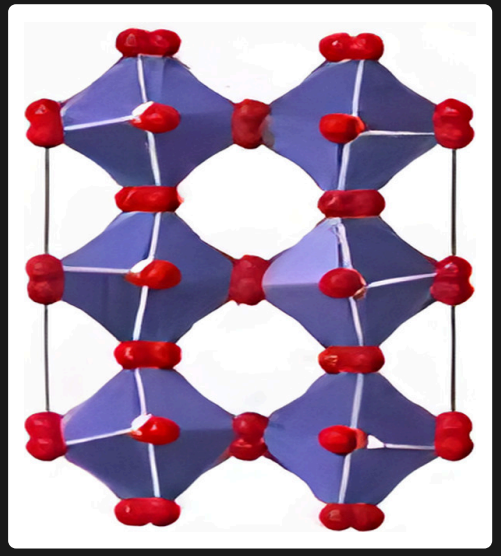


1 > t > 0.9	the undersized A-site cation causes an octahedral tilting distortion
Ti environment	still an octahedron
Ca coordination	reduced to 8

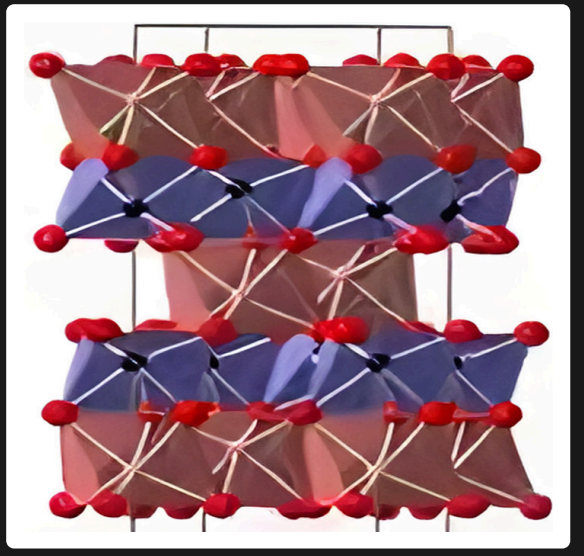
$ATiO_3$ STRUCTURES ($t < 1$)



$SrTiO_3$
t = 1.00
Cubic perovskite
Sr coordination 12



$CaTiO_3$
t = 0.95
Distorted perovskite
Ca coordination ~8



$MgTiO_3$
t = 0.85
Ilmenite
Mg coordination 6

As the tolerance factor falls below 1.00 the octahedra begin to rotate so that some of the anions can maintain contact with the A-site cation. This is called an octahedral tilting distortion. The ilmenite structure emerges when the tolerance factor decreases beyond a certain point.

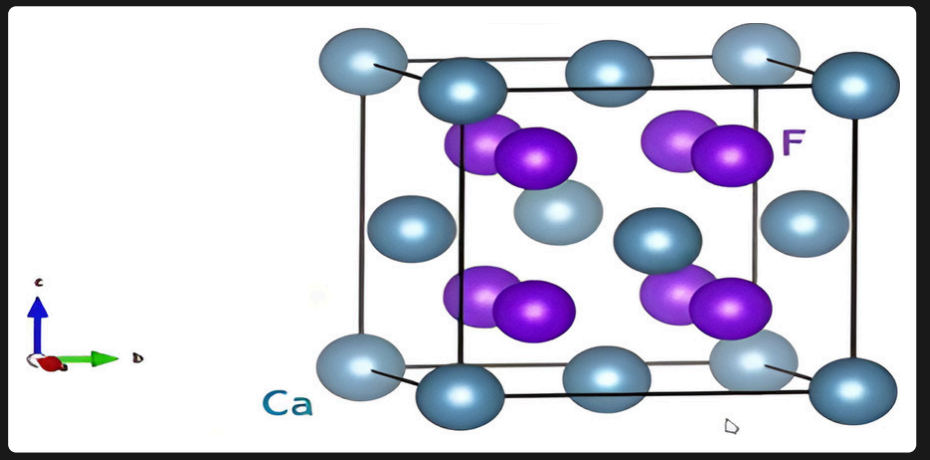
SUMMARY

Spinel, garnet, and perovskite compared on where the cations sit, and perovskite on how the framework responds when the A cation does not fit.

Structure	Formula	Sites and packing	Applications
Spinel	AB_2O_4	ccp O^{2-} lattice; normal versus inverse site distributions	magnetism (Fe_3O_4)
Garnet	$X_3Y_2Si_3O_{12}$	cubic (8), octahedral (6), tetrahedral (4) sites	lasers (Nd:YAG), magnets (YIG), gemstones
Perovskite	ABO_3	corner-sharing BO_6 octahedra, A in 12-coordination; fit measured by the tolerance factor t	ferroelectric $BaTiO_3$; piezoelectrics and dielectrics

CaF_2 (FLUORITE)

Space group	$Fm\bar{3}m$ (#225)			
Lattice parameter	a = 5.46 Å			
Atom	**Wyckoff site**	**x**	**y**	**z**
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



Ca (4a)	0,0,0	½,½,0	½,0,½	0,½,½
F (8c)	¼,¼,¼	¾,¾,¼	¾,¼,¾	¼,¾,¾
	¼,¼,¾	¾,¾,¾	¾,¼,¼	¼,¾,¼

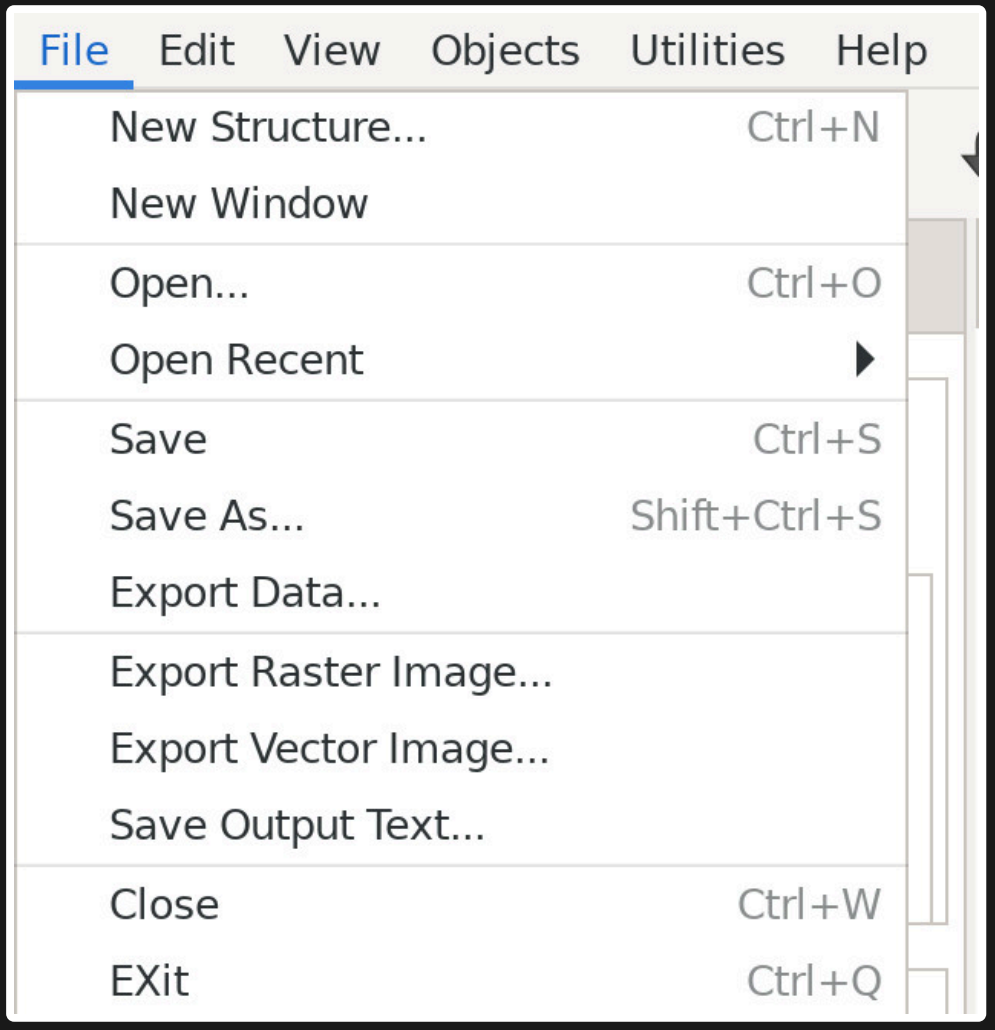
START A NEW STRUCTURE

File → New Structure… (Ctrl+N)

The New Data dialog opens. Use its tabs in this order:

1. **Phase**: name the structure
2. **Unit cell**: set the symmetry and lattice parameters
3. **Structure parameters**: enter the atoms

Go to **Unit cell** first.

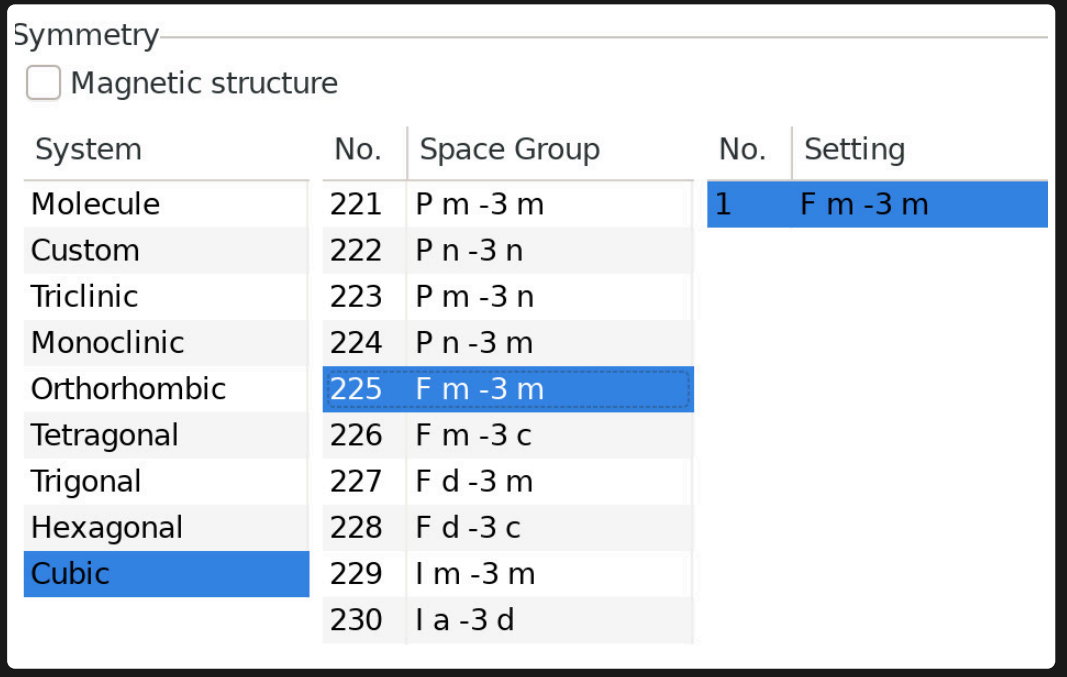


SET THE CRYSTAL SYSTEM AND SPACE GROUP

System	Cubic
Space group	$Fm\bar{3}m$ (#225)

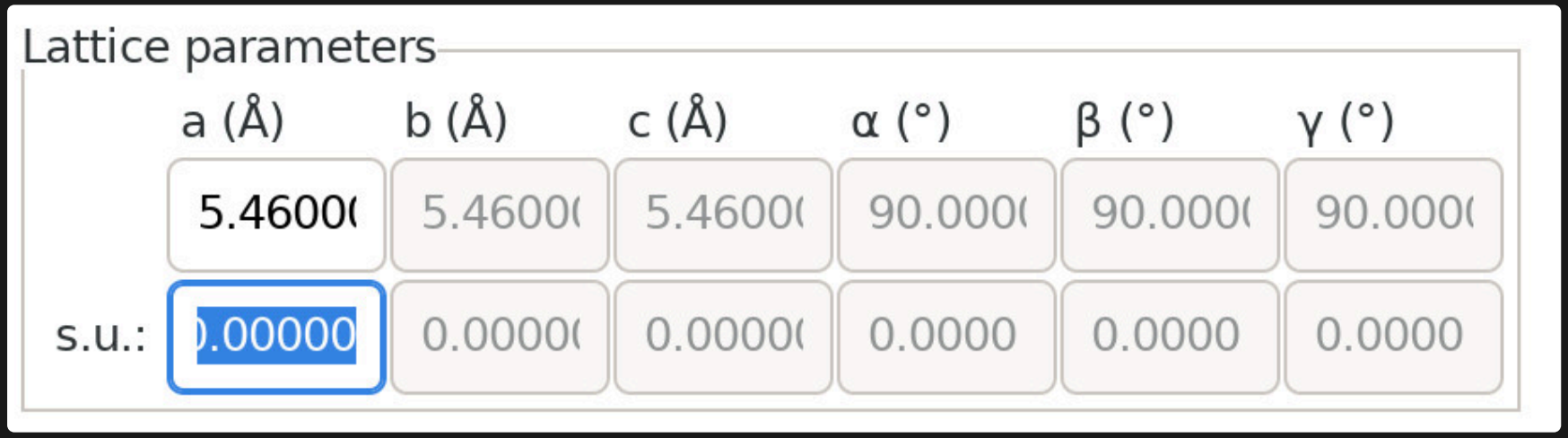
Choose **Cubic** to limit the list to cubic space groups.

Scroll to **225** and click it. Check that the Setting panel shows **setting 1, F m -3 m**.



SET THE LATTICE PARAMETER

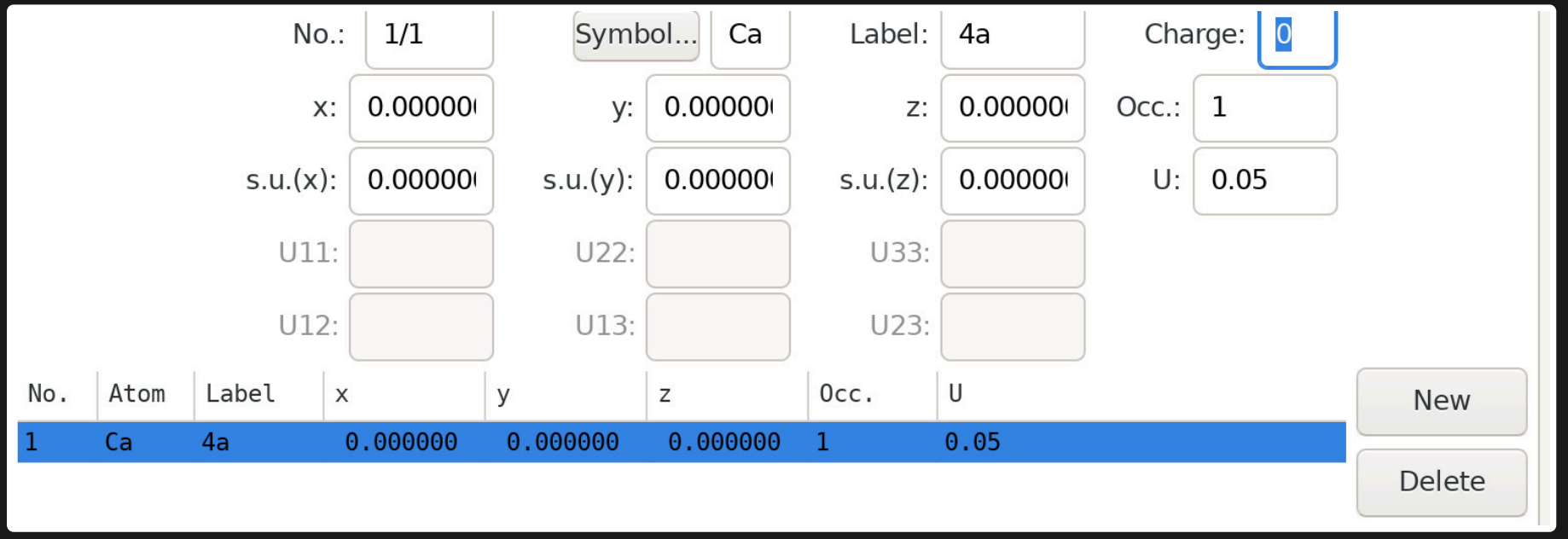
Set **a = 5.46** in the a field at the bottom of the Unit cell tab and press Return. Because the cell is cubic, VESTA **sets b and c automatically** and greys out those fields. The angles remain 90°.



ADD THE CALCIUM SITE

Symbol	Label	x	y	z	Occ.
Ca	4a	0	0	0	1

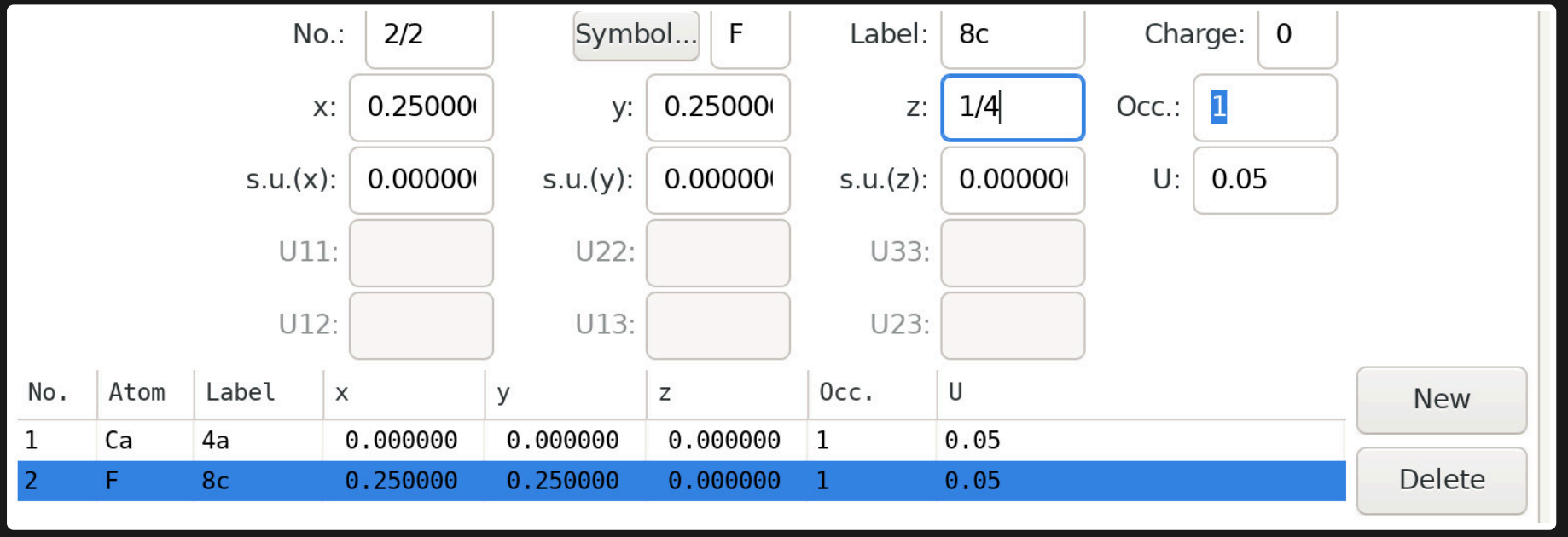
On the **Structure parameters** tab, press **New** and enter the values above. You can choose any Label, but the Wyckoff symbol identifies the site in each row.



ADD THE FLUORINE SITE

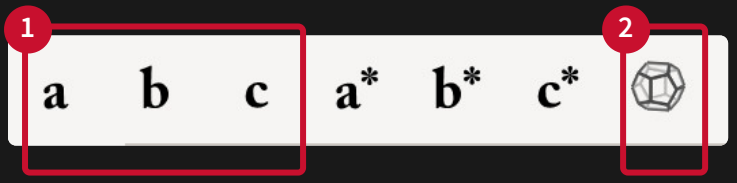
Symbol	Label	x	y	z	Occ.
F	8c	1/4	1/4	1/4	1

Press **New** again. The new row contains the calcium values, so **clear each field before typing**. Enter **1/4** for each coordinate; VESTA stores it as 0.250000. Then press **OK**.

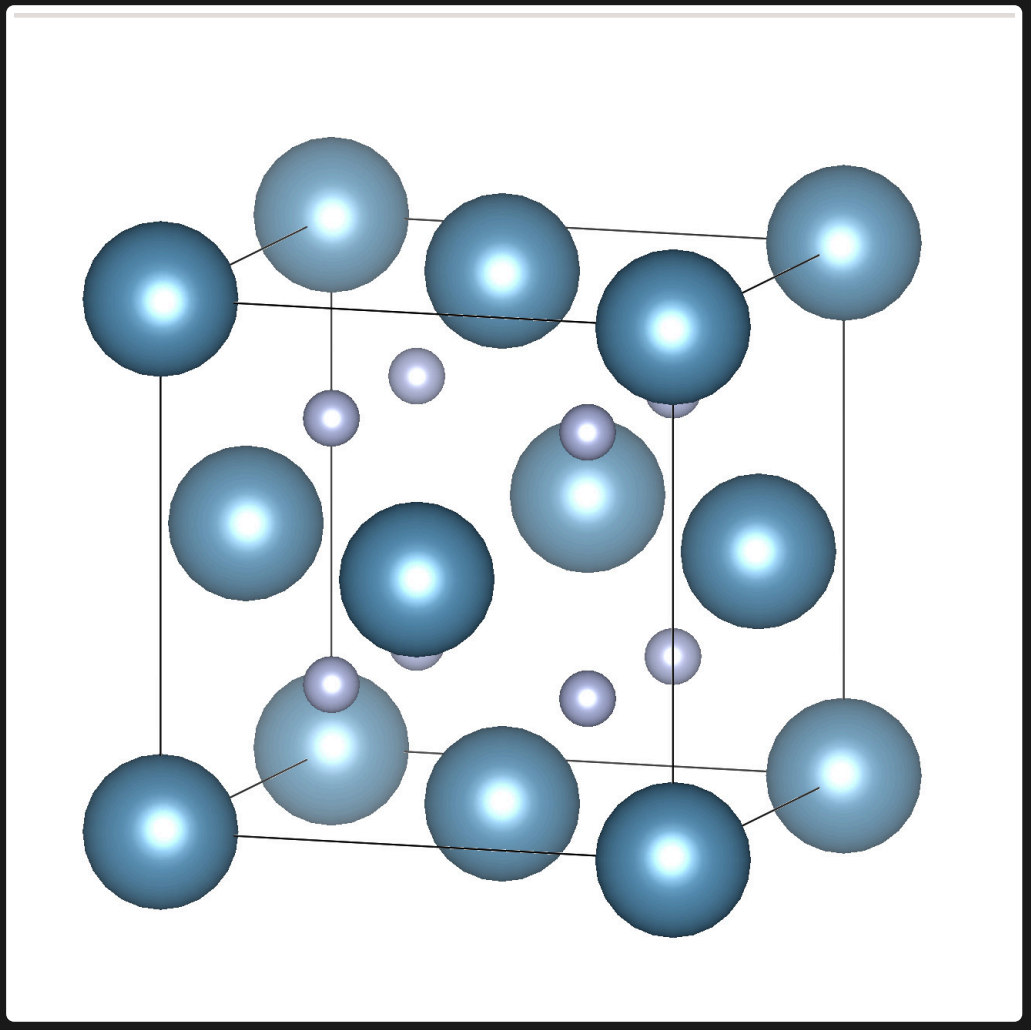


APPLY AND LOOK ALONG THE AXES

1. Use **a, b, c** to look along each axis. For fluorite, the views are **identical** because cubic symmetry makes the axes equivalent.
2. Choose **Standard orientation** to tilt the cell and see every atom at once.



Large spheres are Ca; small spheres are F.



READ THE STRUCTURE OUTPUT

Check the structure data in the output panel. The last two columns list the **generated Wyckoff sites**; the last line gives the **number of atoms drawn**.

Count the Ca and F atoms in one unit cell.

4 Ca and 8 F.

VESTA includes atoms on the cell boundary, so it draws 14 Ca:
8 corners × ⅛ + 6 faces × ½ = **4**.
All 8 F lie entirely inside, giving **8**.

```
================================================================================
Title               New structure

Lattice type        F
Space group name    F m -3 m
Space group number  225
Setting number      1

Lattice parameters

   a        b        c       alpha    beta     gamma
 5.46000  5.46000  5.46000  90.0000  90.0000  90.0000

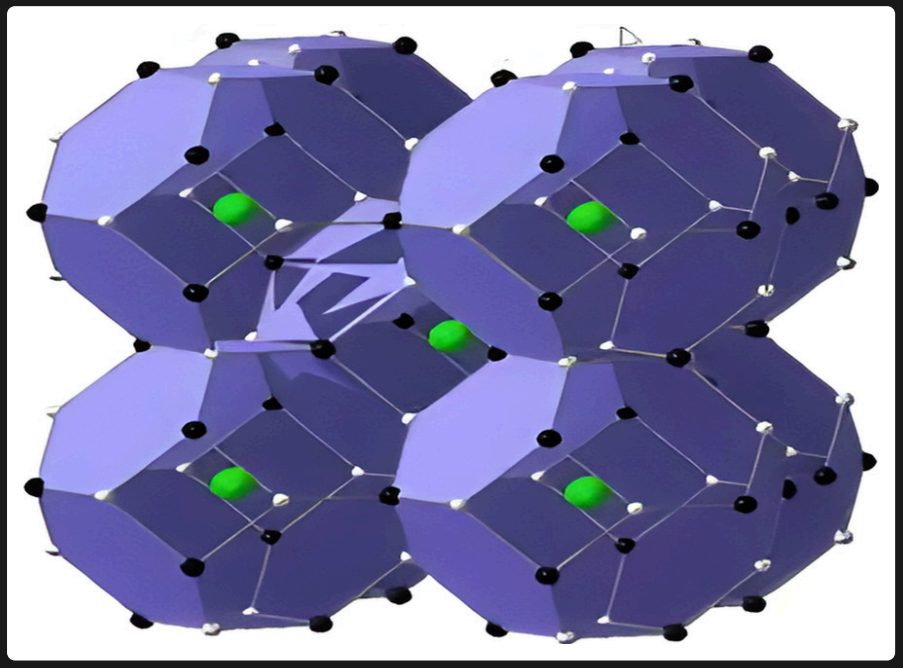
Unit-cell volume = 162.771339 Å^3

Structure parameters

                       x          y          z          Occ.     U    Site      Sym.
   1 Ca  4a          0.00000    0.00000    0.00000    1.000    0.050    4a      m-3m
   2 F   8c          0.25000    0.25000    0.25000    1.000    0.050    8c      -43m
================================================================================

Number of polygons and unique vertices on isosurface = 0 (0)
22 atoms, 0 bonds, 0 polyhedra; CPU time = 0 ms
```

SODALITE – $Na_8Al_6Si_6O_{24}Cl_2$



Cage packing — the cages share hexagonal faces (6-rings) in a body-centered cubic arrangement

Openings — 6 tetrahedra around the ring, about 2.6 Å; guest molecules cannot get in or out (not microporous)

Space group $P\bar{4}3n$, a = 8.875 Å

Na1	8e	0.1777(2)	0.1777(2)	0.1777(2)
Al1	6d	1/4	0	1/2
Si1	6c	1/4	1/2	0
O1	24i	0.1387(3)	0.1484(3)	0.4375(2)
Cl1	2a	0	0	0

READING A SHORT SYMBOL

Crystal system	Shape	Its point groups	What the positions mean, in order
Triclinic	all skew	1, $1\bar{}$	no direction to name
Monoclinic	one lean	2, m, 2/m	one direction: **b**
Orthorhombic	a brick	222, mm2, mmm	**a**, then **b**, then **c**
Tetragonal	square column	4, $4\bar{}$, 4/m, 422, 4mm, $\bar{4}2$m, 4/mmm	**c**; then **a** and **b**; then the in-plane diagonals
Trigonal & hexagonal	120° base	3, $3\bar{}$, 32, 3m, $\bar{3}$m; 6, $6\bar{}$, 6/m, 622, 6mm, $\bar{6}$m2, 6/mmm	**c**; then the cell edges; then the in-plane diagonal
Cubic	a die	23, m$3\bar{}$, 432, $\bar{4}3$m, m$\bar{3}$m	the cell edges; then the body diagonals; then the face diagonals

Per *Solid State Materials Chemistry*, §1.1.3, Table 1.1 and §1.1.7, Table 1.3.

1. Crystal system — write every glide as m and every screw as its rotation, then match what is left against a row above: **mma** becomes mmm, orthorhombic. A 3 in the first position is trigonal, in the second cubic

2. Bravais lattice — the leading letter is the centering, and system plus letter name the lattice; a trigonal group under **P** sits on the primitive hexagonal lattice, under **R** on the rhombohedral

3. Point group — the replaced symbol of step 1, without its lattice letter, is the point group

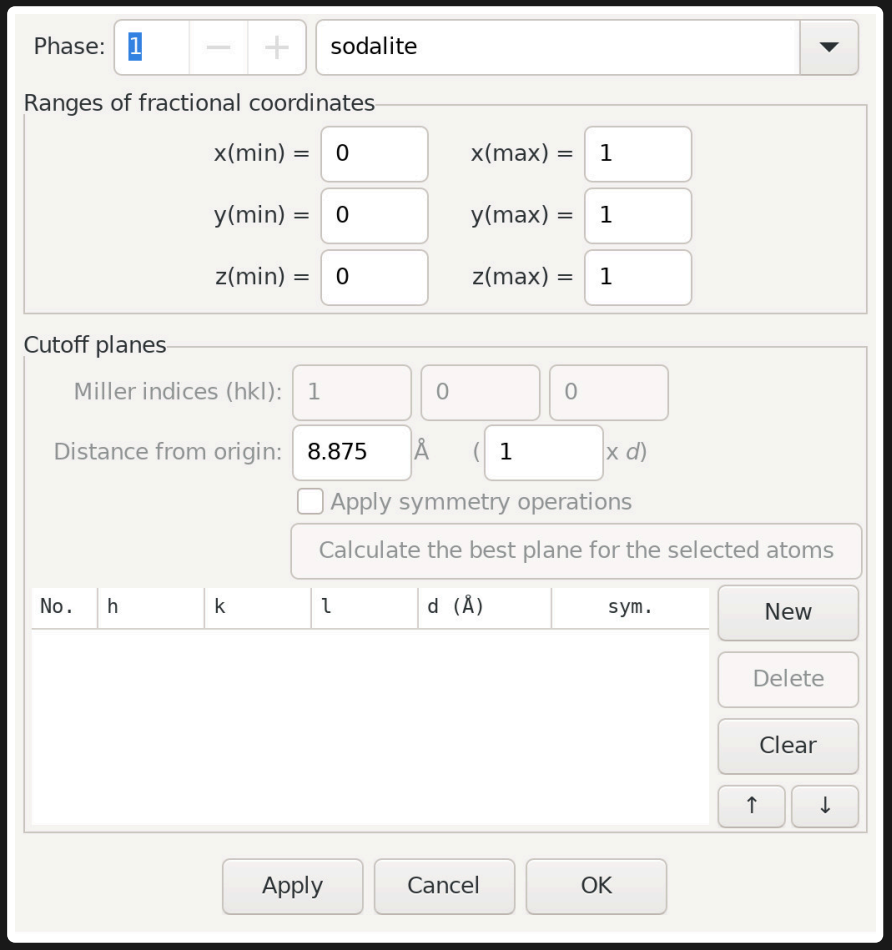
4. Symmorphic? — if you replaced anything in step 1, the symbol carries a glide or a screw and the group is non-symmorphic

SHOW ONE SODALITE CAGE

Start with the sodalite structure entered above.

Open **Objects → Boundary…**. Set all three ranges to **0–1**, then click **OK**.

Use one cell for this view. A 3 × 3 × 3 block contains many overlapping cages.



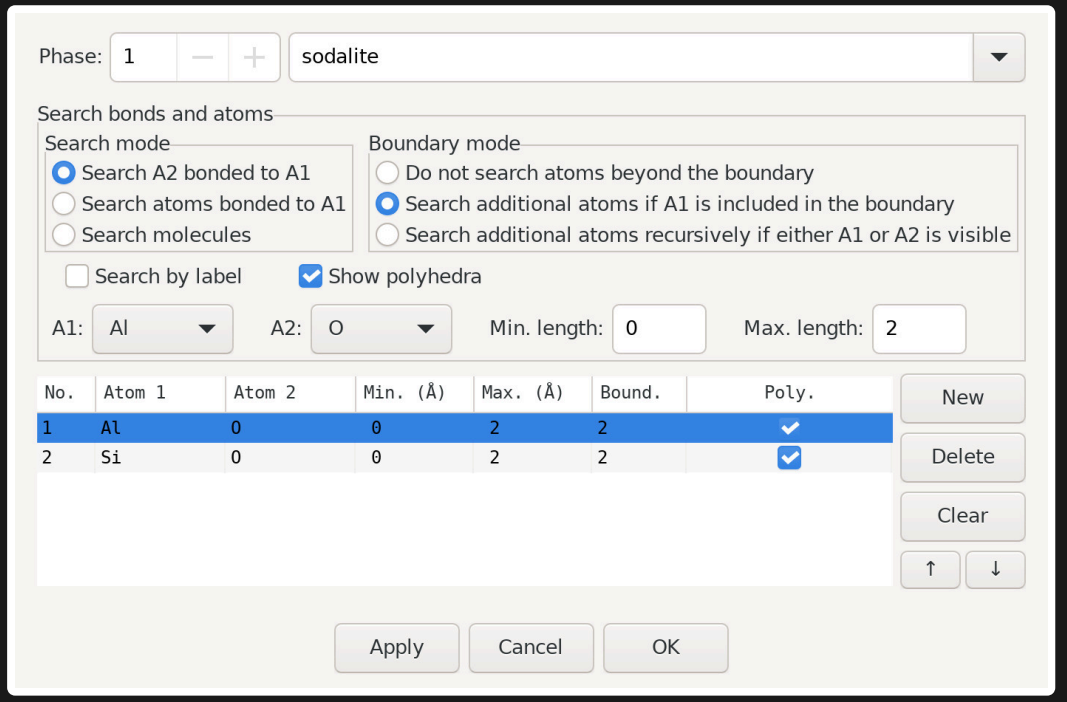
DEFINE THE TWO TETRAHEDRAL UNITS

Open **Edit → Bonds…**. For this view, keep only these two entries; use **New** to add any missing row.

A1	A2	Min. Å	Max. Å
Al	O	0	2.0
Si	O	0	2.0

For both rows, tick **Show polyhedra** and select **Search A2 bonded to A1**.

Under Boundary mode, choose **Search additional atoms if A1 is included in the boundary**. Click **OK**.

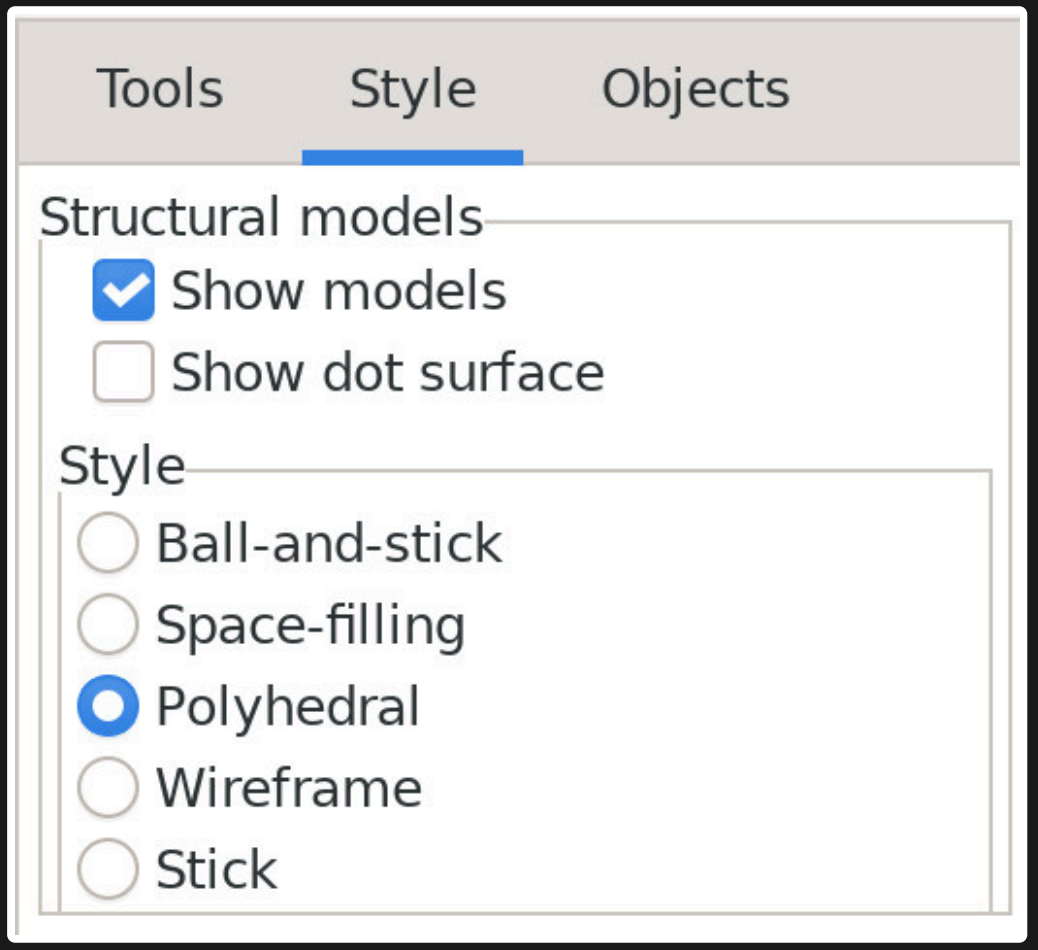


SWITCH TO THE POLYHEDRAL DISPLAY

In the left panel, open **Style** and select **Polyhedral**.

Check that both AlO_4 and SiO_4 tetrahedra appear.

If one set is missing, return to **Edit → Bonds…** and check that row's **2.0 Å** limit and **Show polyhedra** box.



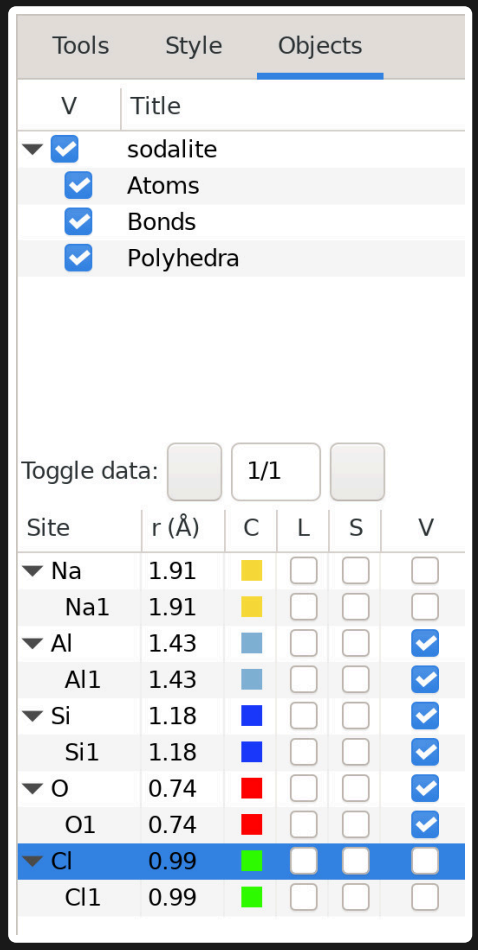
HIDE THE IONS INSIDE THE CAGES

Open the **Objects** tab in the left panel and select **Atoms**.

In the **V** column, clear the checkboxes for **Na** and **Cl**. Keep **Al, Si and O** visible.

To hide the cell edges, open **Properties… → General** and choose **Unit cell → Do not show**.

This changes the display, not the structure.



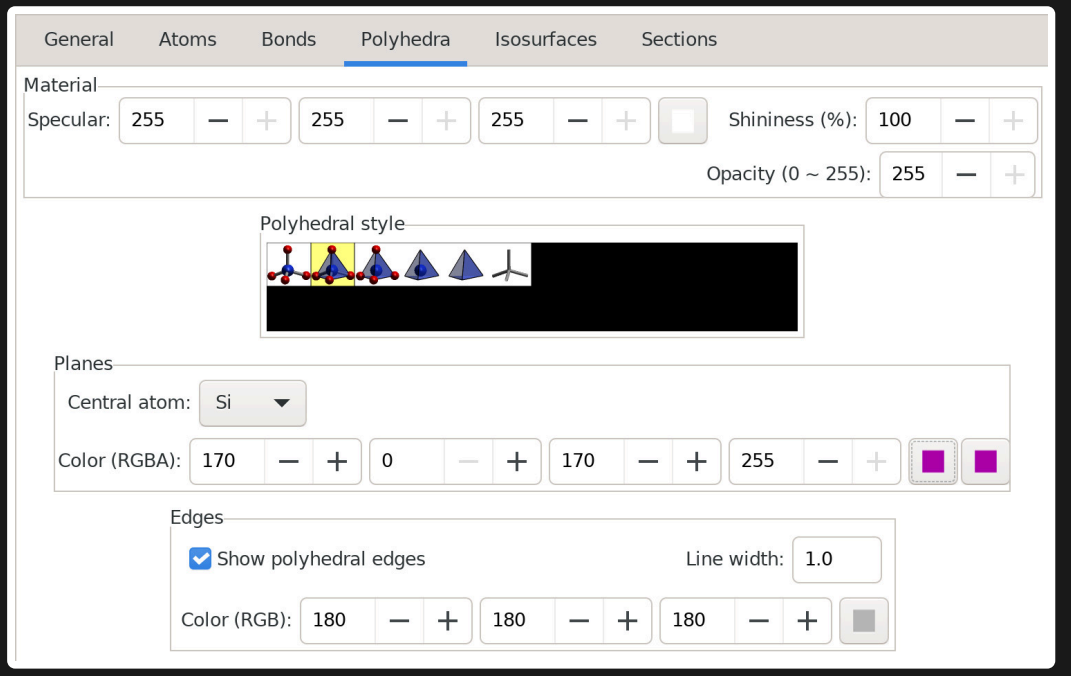
DISTINGUISH ALUMINUM AND SILICON

Open **Properties… → Polyhedra**. Under **Planes**, choose each **Central atom** and enter its **Color (RGBA)**.

Centre	R	G	B	A
Al	160	160	160	255
Si	170	0	170	255

AlO_4 is **grey**; SiO_4 is **purple**. An alpha value of **255** makes the faces opaque.

Keep **Show polyhedral edges** checked, then click **OK**.

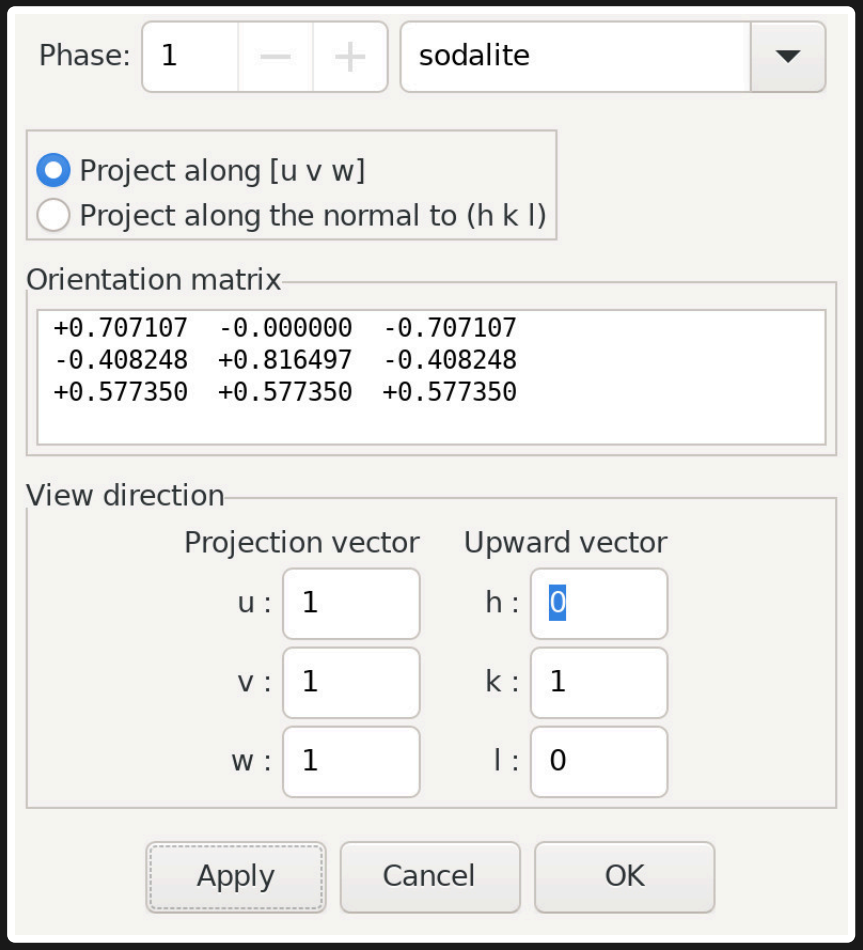


LOOK THROUGH A HEXAGONAL OPENING

Click **Orientation…**. Select **Project along [u v w]** and set the projection vector to **1, 1, 1**.

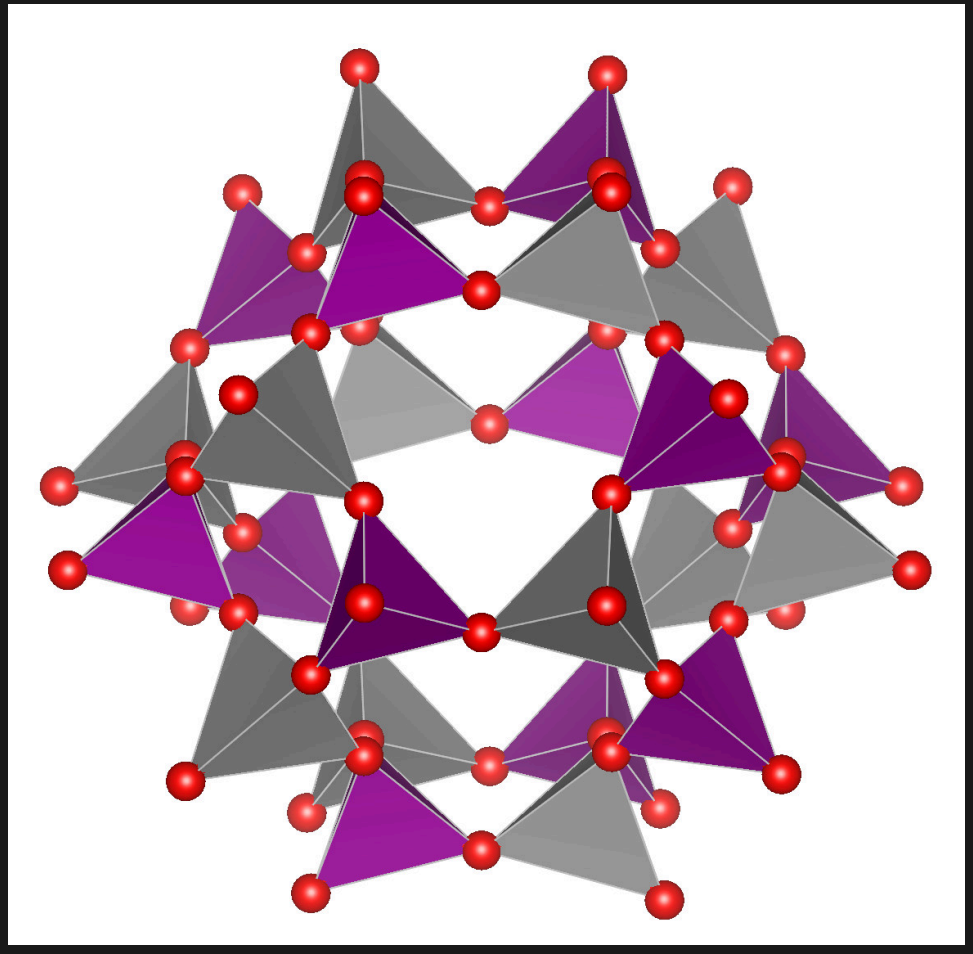
Leave the upward vector at **0, 1, 0**, then click **OK**.

To separate the front and back tetrahedra, set **Step (°) = 15** and click the **first curved rotation arrow** once.



THE SODALITE CAGE IN VESTA

Grey AlO_4 and purple SiO_4 tetrahedra share red oxygen corners.



Na and Cl are hidden in this view. Save the display with **File → Save As… → VESTA format**.

PROBLEM 1.18: STACKING IN TERBIUM

With a structure-drawing program, determine the stacking sequence in Tb. Suggest the Ramsdell symbol and the Jagodzinski–Wyckoff notation.

$P6_3/mmc$ (194), hexagonal

a = b = 3.068 Å; c = 14.87 Å; α = β = 90°, γ = 120°

Atom	Site	x	y	z
Tb	2b	0	0	¼
Tb	4f	⅓	⅔	0.083

Build the structure, look down c, then turn the cell to see the layers along c. Label their lateral positions A, B and C.

SSMC, Problem 1.18; data reproduced in the Lecture 7 VESTA tutorial.

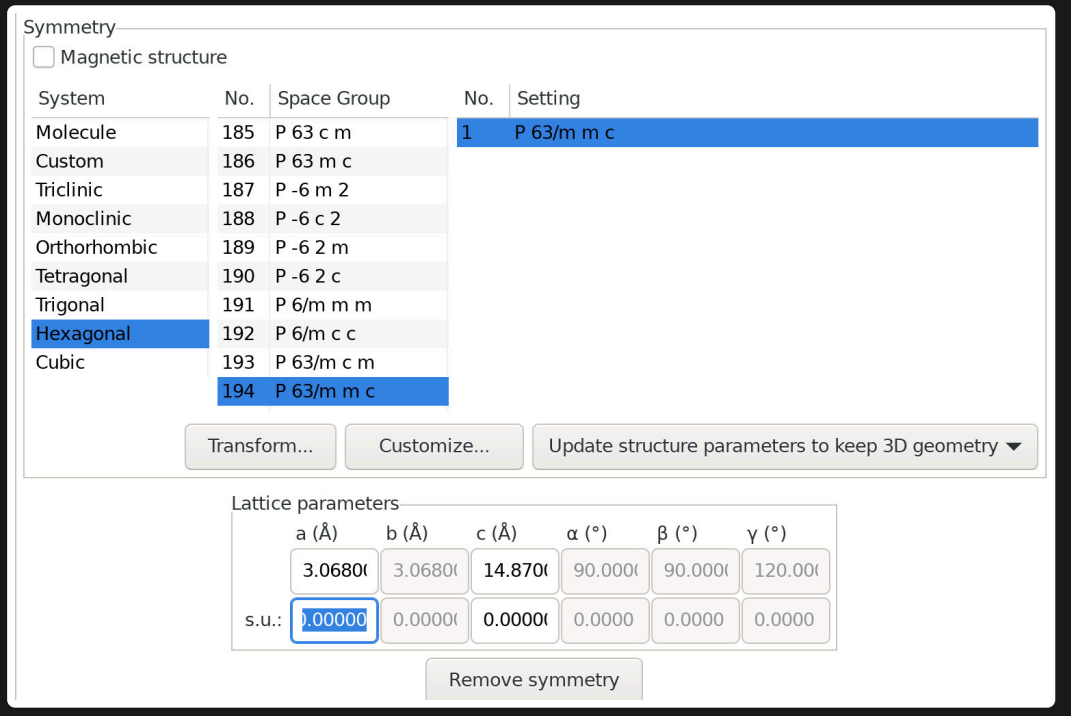
BUILD THE HEXAGONAL TB CELL

Choose **File → New Structure…**, then **Unit cell**.

Select **Hexagonal** and space group **194, $P6_3/mmc$**.

Parameter	Value
a = b	3.068 Å
c	14.87 Å
α = β	90°
γ	120°

Enter a and c. The symmetry fixes b and the angles.



ENTER TWO INDEPENDENT TB SITES

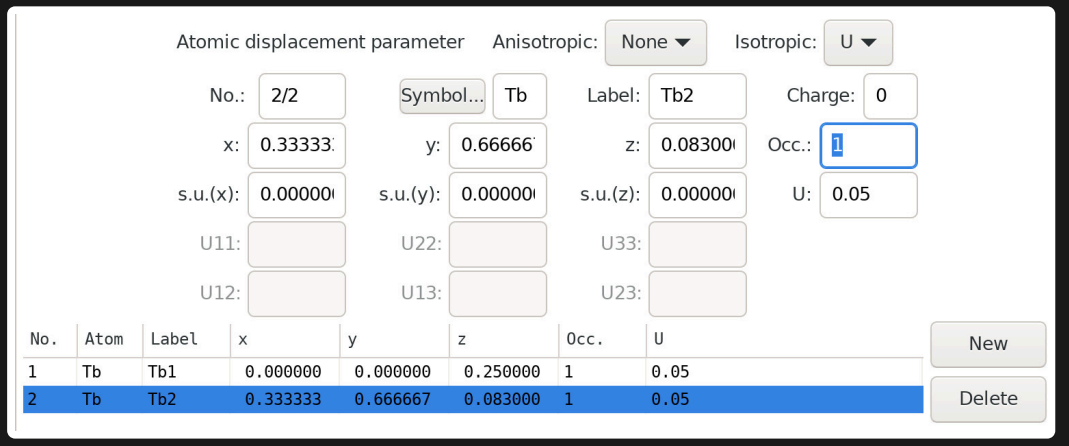
Open **Structure parameters**. Click **New** for each row.

Label	Symbol	x	y	z
Tb1	Tb	0	0	0.25
Tb2	Tb	1/3	2/3	0.083

Leave both occupancies at **1**, then click **OK**.

Check the **Output** pane: Tb1 is **2b**, Tb2 is **4f**.

2 + 4 = 6 Tb atoms per cell.



KEEP ONE REPRESENTATIVE OF EACH POSITION

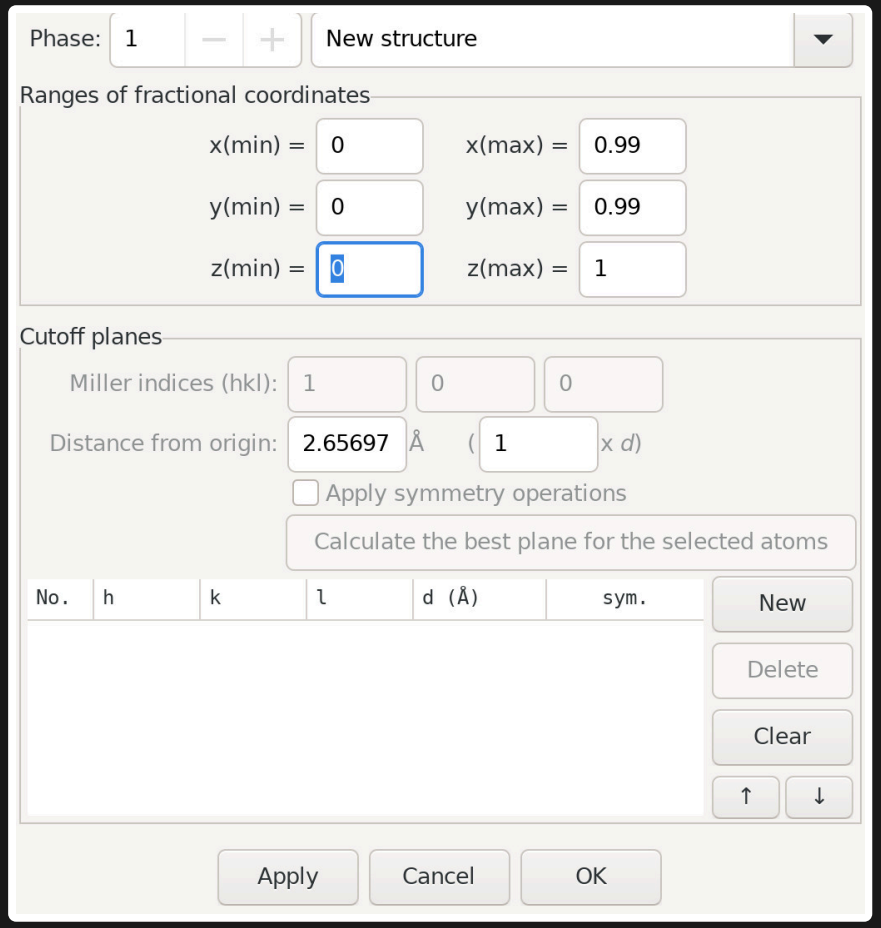
Open **Objects → Boundary…**.

Range	Minimum	Maximum
x	0	0.99
y	0	0.99
z	0	1

Leave **Cutoff planes** empty and click **OK**.

Select **Style → Ball-and-stick**.

The display now contains **six atoms**.
Each represents one layer in the stack.



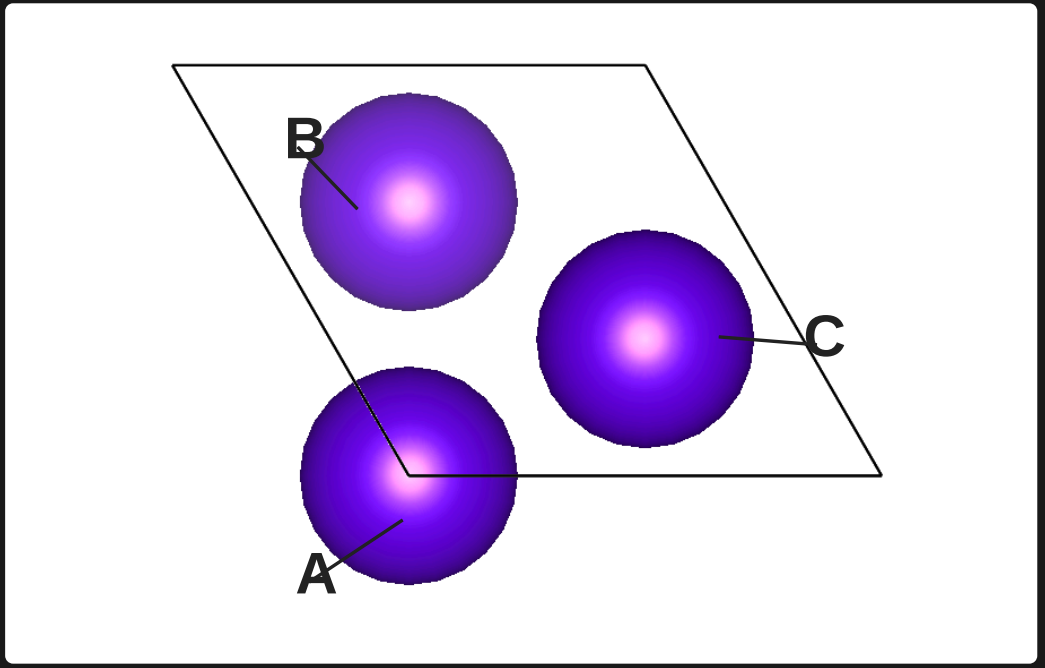
LOOK DOWN C TO LABEL A, B AND C

Click the **c** button on the top toolbar to view along **[001]**.

Use the mouse wheel or **+** to enlarge the model.

Position	x	y
A	0	0
B	1/3	2/3
C	2/3	1/3

The three spots are **columns of overlapping Tb atoms**. This view identifies positions, but hides their order along c.



TURN THE SIX LAYERS UPRIGHT

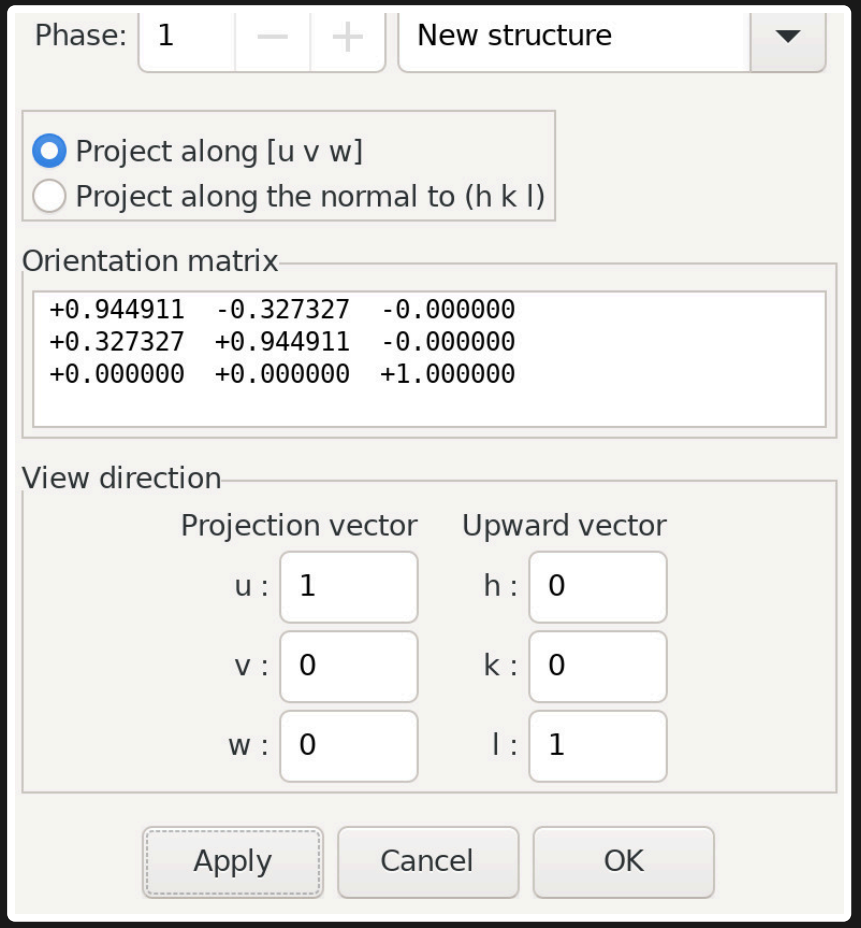
Click **Orientation…** and choose **Project along [u v w]**.

Vector	Values
Projection	1, 0, 0
Upward	0, 0, 1

Click **OK**. Use the top-toolbar **fit-to-screen** button if needed.

View along a, [100].
c, [001], points up.

The (001) layers are now seen edge-on.



READ THE STACKING FROM BOTTOM TO TOP

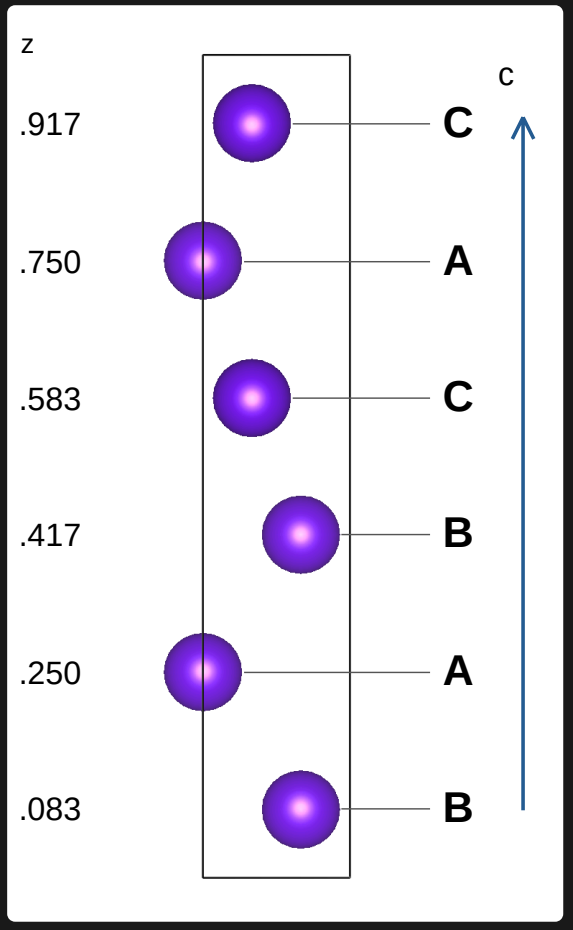
View [100]; c points up.

z	Position
0.083	B
0.250	A
0.417	B
0.583	C
0.750	A
0.917	C

Follow the column positions upward:

B → A → B → C → A → C

Each atom represents a whole close-packed layer. The next cell repeats the sequence.



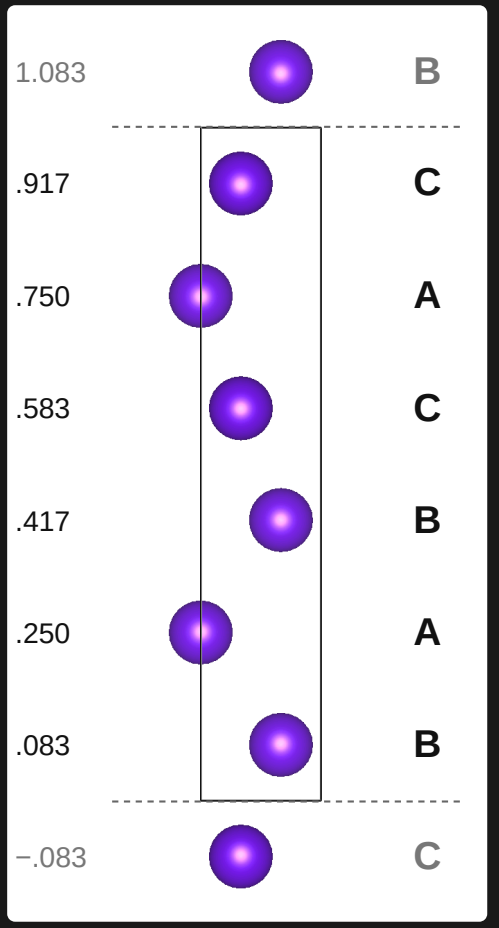
INCLUDE NEIGHBOURS ACROSS THE CELL BOUNDARY

Return to **Boundary…**. Keep x and y unchanged; extend **z from −0.10 to 1.10**.

Click **OK** and fit the model to the window.

Layer to classify	Below	Above
First B, z = 0.083	C, z = −0.083	A, z = 0.250
Last C, z = 0.917	A, z = 0.750	B, z = 1.083

The two extra atoms belong to **adjacent cells**. They do not increase the six-layer repeat.



ASSIGN H OR C TO EACH LAYER

Compare the layers immediately **below and above the layer being classified**.

Same position → h. For B–**A**–B, the middle A is h.
Different positions → c. For A–**B**–C, the middle B is c.

z	Below	Layer	Above	Label
0.083	C	B	A	c
0.250	B	A	B	h
0.417	A	B	C	c
0.583	B	C	A	c
0.750	C	A	C	h
0.917	A	C	B	c

Bottom to top: **c h c c h c**.
Start at an A layer instead: **h c c h c c** = $(\mathbf{hcc})_2$.

PROBLEM 1.18: CHECK THE TWO SYMBOLS

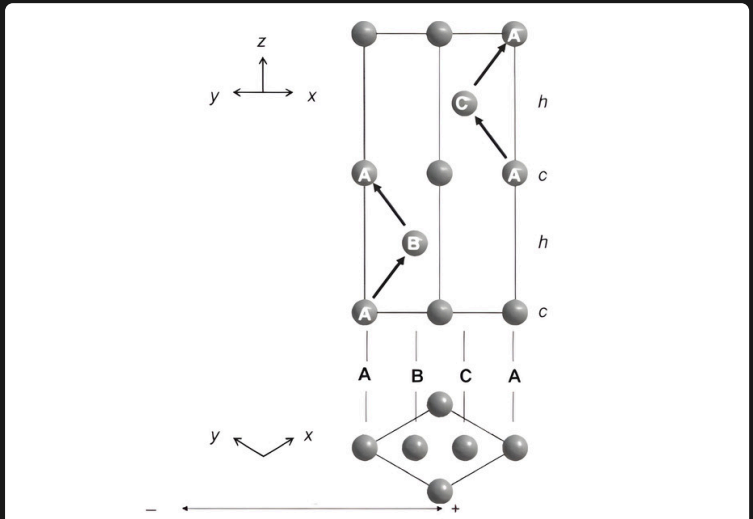
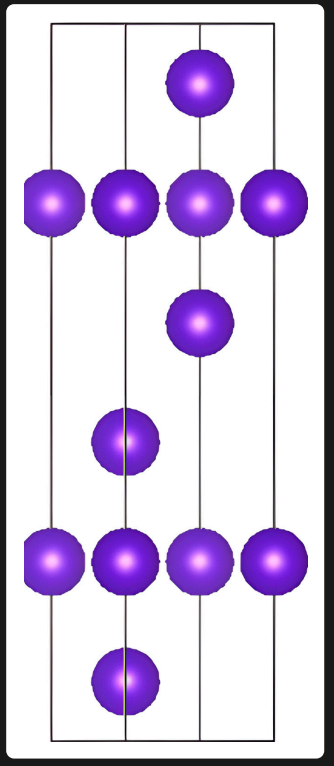


Figure 1.22 How to analyze sphere packing in hexagonal structures (α-La shown).



Tb

C c

A h

C c

B c

A h

B c

6H · (hcc)₂

Ramsdell symbol	4H
Jagodzinski–Wyckoff notation	$(hc)_2$
ICSD #102655	$P6_3/mmc$ (194) hexagonal, a = 3.770 Å, c = 12.159 Å; La on 2a (0, 0, 0) and 2c (1/3, 2/3, 1/4)

Per *Solid State Materials Chemistry*, Figure 1.22 and Problem 1.18.

PROBLEM 1.31: HOLE FILLING IN SPINEL

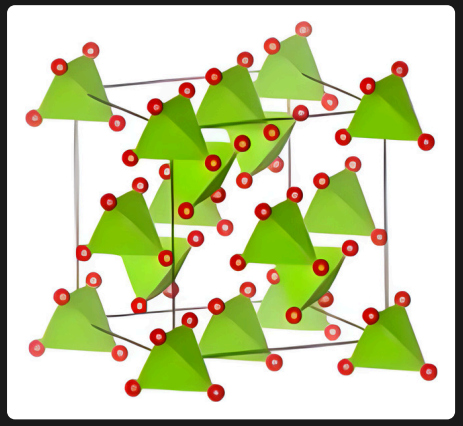
Analyze hole filling in the spinel structure of cubic close-packed oxygens.

1. Given the general formula $[\text{tetrahedron}]_1[\text{octahedron}]_2O_4$, calculate the total fractions of tetrahedral and octahedral holes filled.
2. Use a structure-drawing program to orient the structure and identify the type of filled holes between layers of densely packed oxygen atoms.
3. Determine the sequence and the fraction of each hole filling.

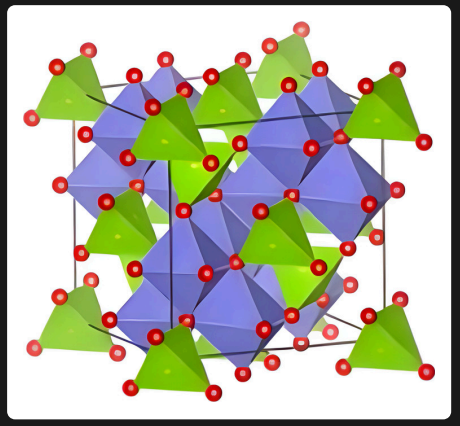
Use the $MgAl_2O_4$ structure from the start of this lecture. Look along [111] to identify the oxygen layers, then turn the model to see the spaces between them.

SSMC, Problem 1.31; Lecture 7 VESTA tutorial.

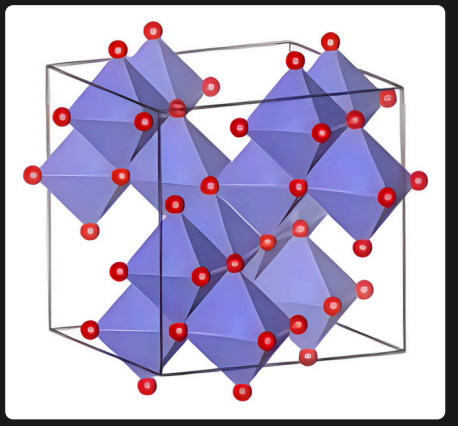
SPINEL STRUCTURE



MgO_4 tetrahedra not connected



ccp array of O; Al in 1/2 octahedral holes; Mg in 1/8 tetrahedral holes



AlO_6 octahedra share edges

$$A^{[4]}B_2^{[6]}O_4^{[1,3]}$$

Normal spinel (e.g. $MgAl_2O_4$)	A tetrahedral (Mg), B octahedral (Al)
Inverse spinel (e.g. $TiFe_2O_4$)	B tetrahedral (Fe); B and A randomly octahedral (Fe, Ti)

BUILD SPINEL WITH ORIGIN CHOICE 1

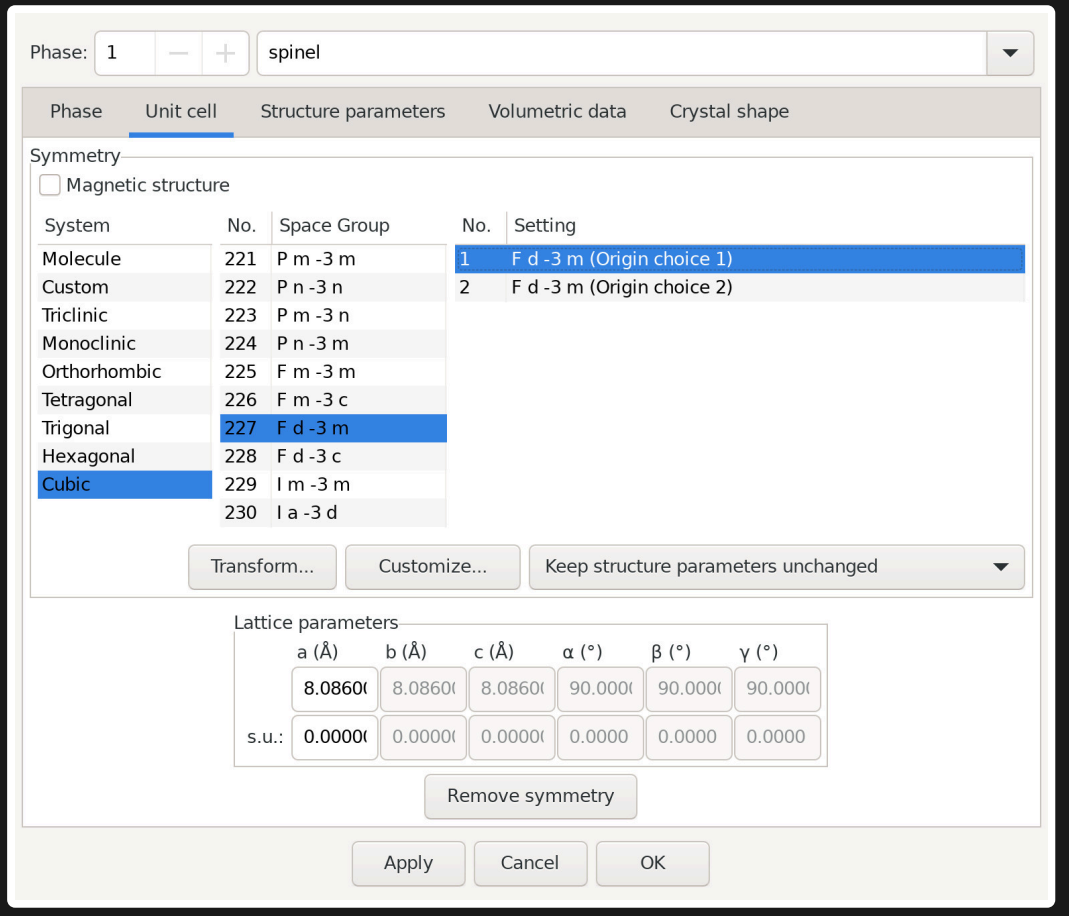
Choose **File → New Structure… → Unit cell**.

Select **Cubic**, then **227, Fd$\bar{3}$m**.

Choose **Origin choice 1** before entering the atoms.

Enter **a = 8.086 Å**. The other edges follow; all angles are 90°.

The coordinates on the next slide use this origin.



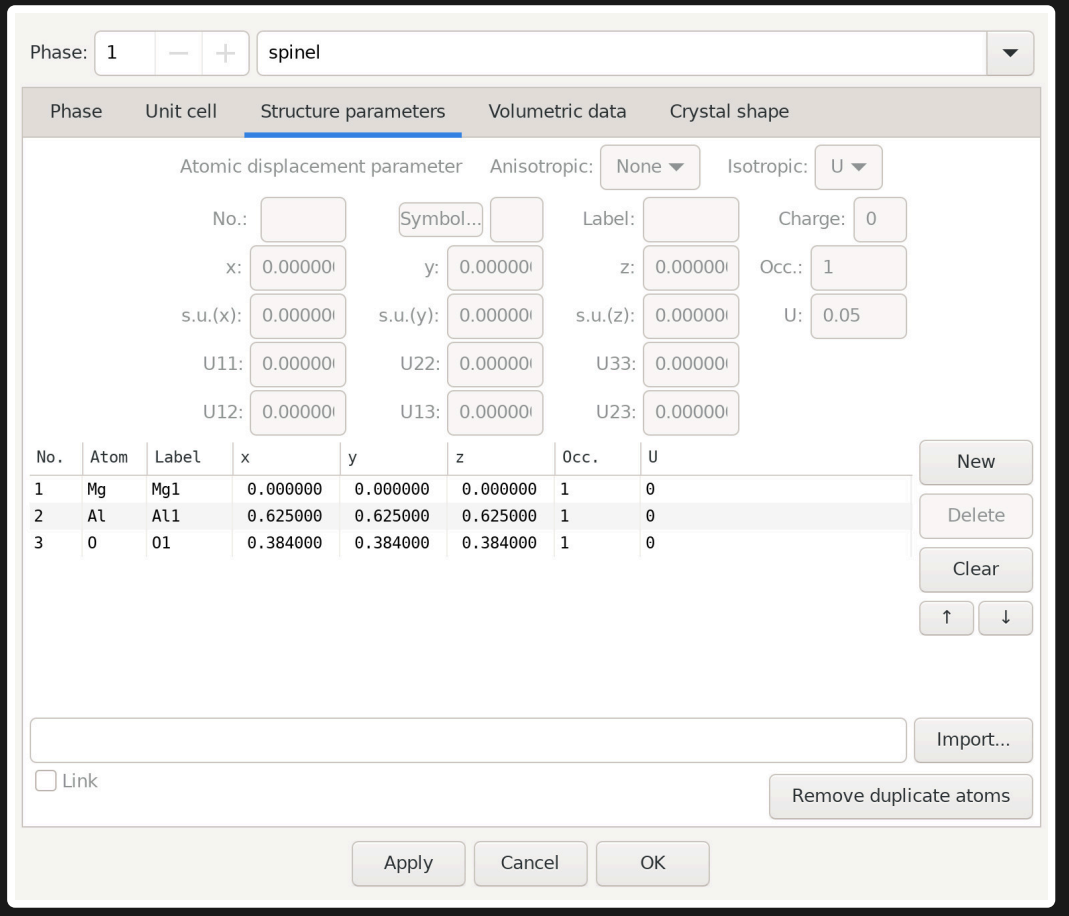
ENTER THE THREE INDEPENDENT SITES

Open **Structure parameters**. Click **New** for each row; keep occupancy at **1**.

Atom	Site	x = y = z
Mg	8a	0
Al	16d	5/8
O	32e	0.384

Click **OK**, then the **standard-orientation** button.

One cell contains **8 Mg, 16 Al and 32 O**, or eight $MgAl_2O_4$ formula units.



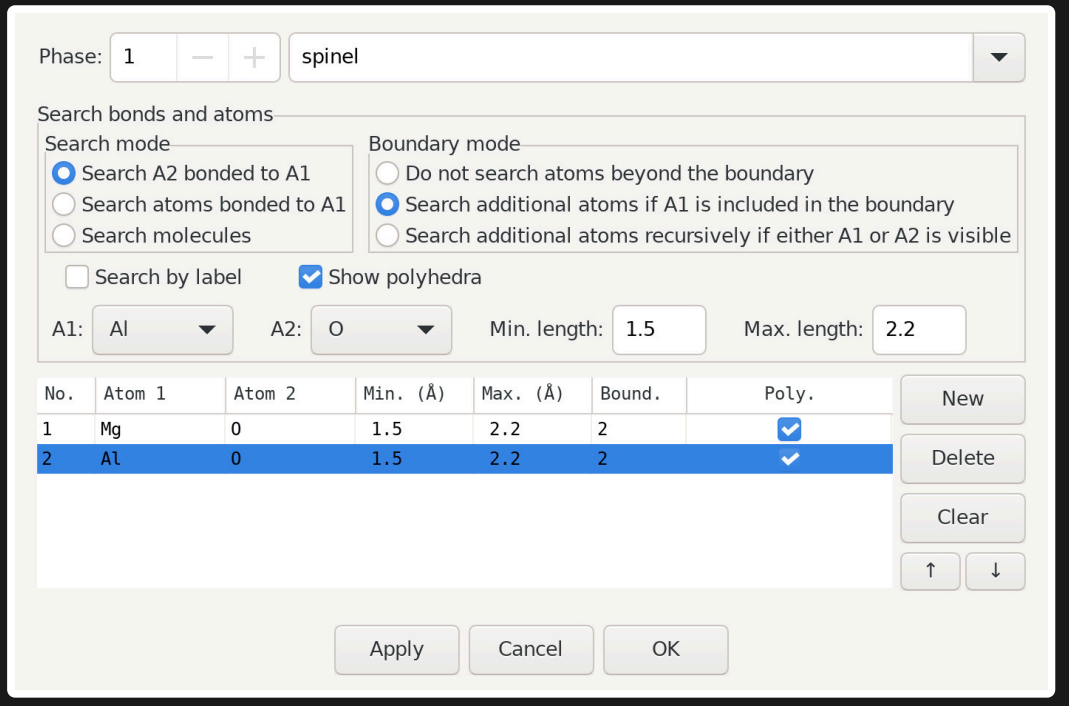
ADD MG–O AND AL–O BONDS

Open **Edit → Bonds…**. Keep only these two rows.

A1	A2	Min. Å	Max. Å
Mg	O	1.5	2.2
Al	O	1.5	2.2

For each row: **Search A2 bonded to A1**, **Show polyhedra**, and **Search additional atoms if A1 is included in the boundary**.

Click **OK**, then **Style → Polyhedral**.



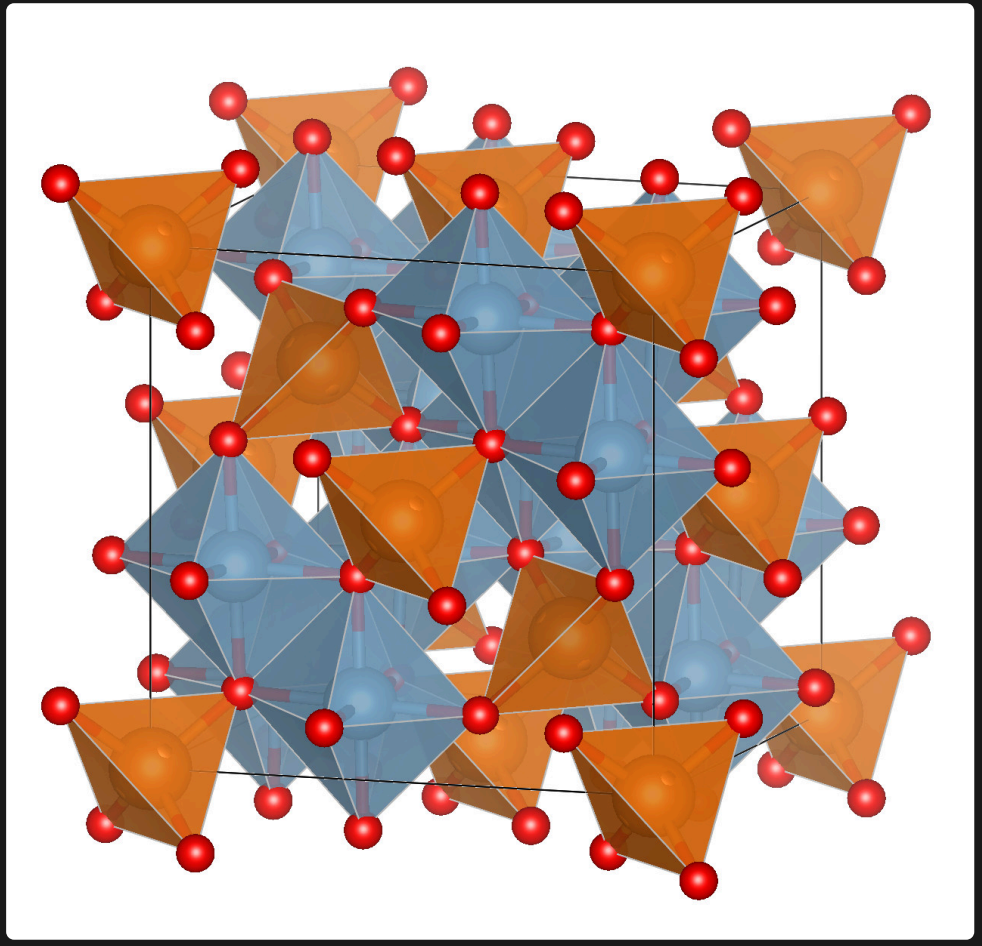
CHECK THE COORDINATION POLYHEDRA

Orange MgO_4 tetrahedra have four oxygen corners.

Blue AlO_6 octahedra have six oxygen corners.

Red spheres are oxygen. These identify the **filled tetrahedral and octahedral holes**.

For 32 O: **64 tetrahedral holes** and **32 octahedral holes**.
Mg fills 8/64 = **⅛**; Al fills 16/32 = **½**.



TURN THE OXYGEN LAYERS SIDEWAYS

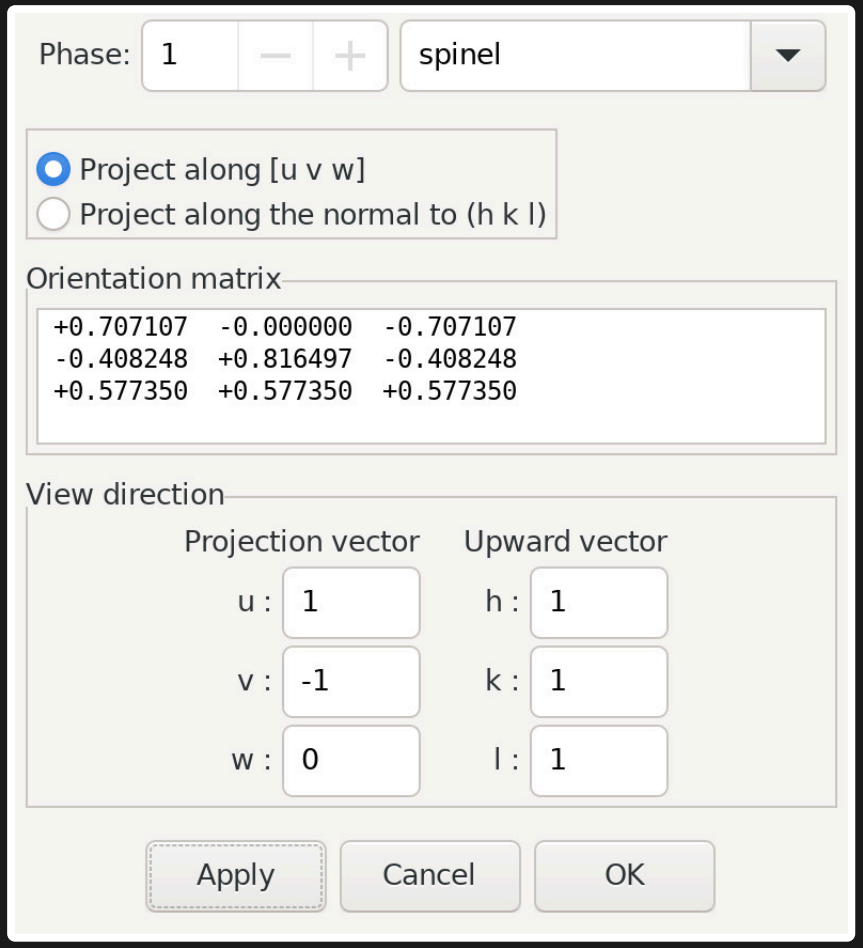
Select **Style → Ball-and-stick**, then click **Orientation…**.

Choose **Project along [u v w]**.

Vector	Values
Projection	1, −1, 0
Upward	1, 1, 1

Click **OK**. The stacking direction [111] now points up.

In **Properties → General**, hide the unit-cell outline with **Do not show**.



↑ [111]
Up: layer stacking

→ [1 1 −2]
Right: along a layer

View along [1 −1 0]
(111) oxygen layers seen edge-on

CUT OUT TWO INTERLAYER REGIONS

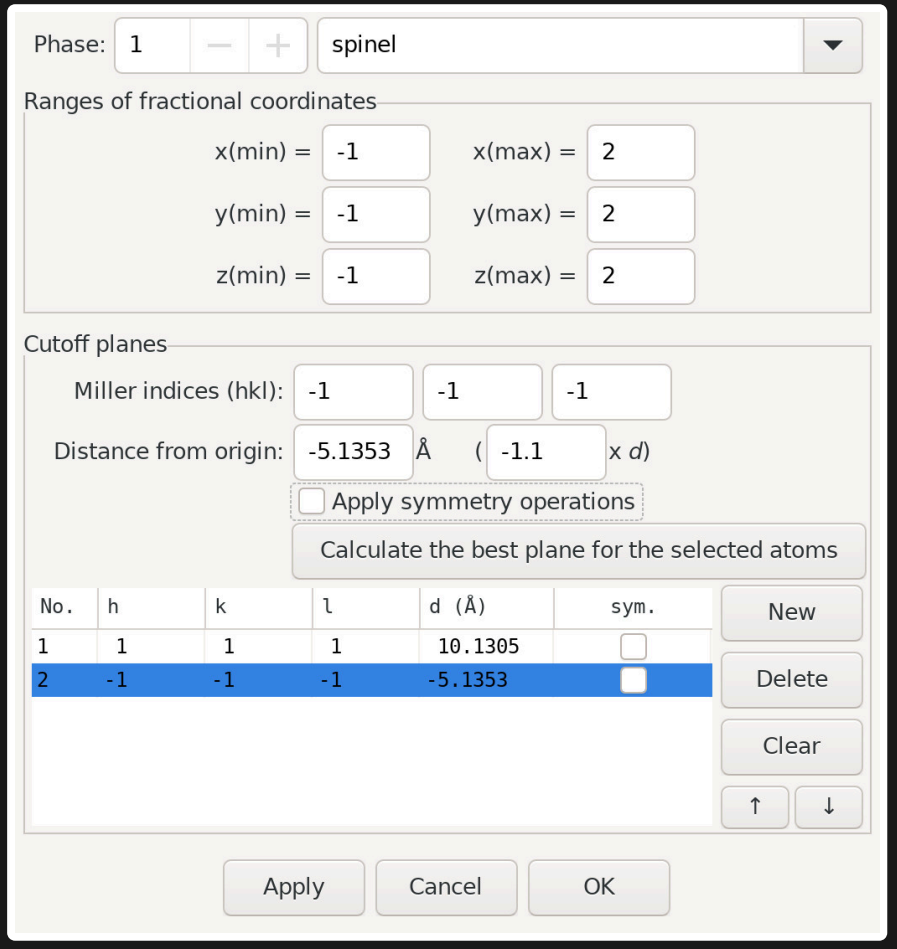
Open **Objects → Boundary…**. Set x, y and z to **−1 through 2**.

Under **Cutoff planes**, click **New** twice and enter:

h, k, l	Distance: × d
1, 1, 1	2.17
−1, −1, −1	−1.10

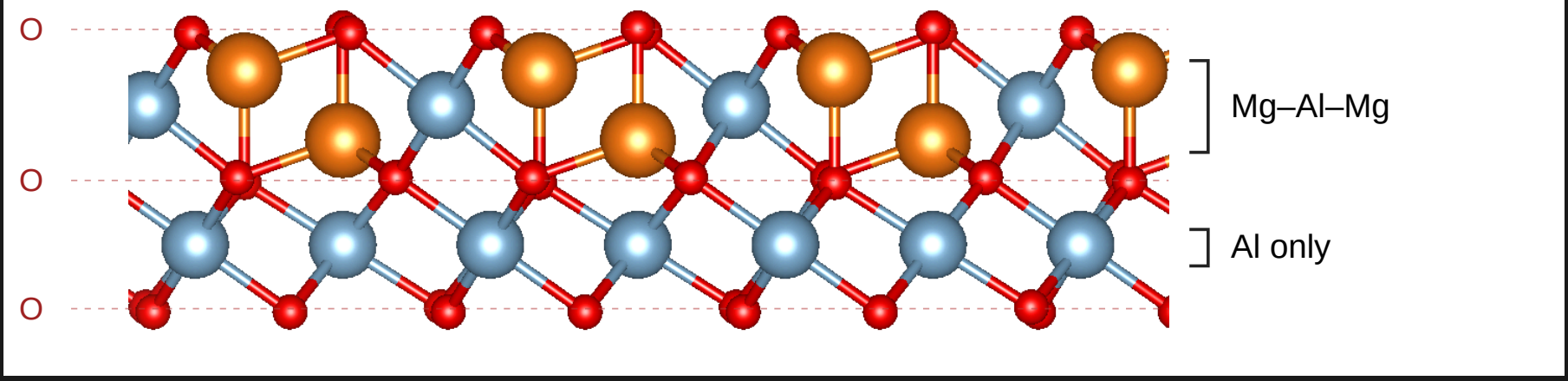
Use the **× d field**, not the Å field. Leave **Apply symmetry operations** unchecked.

Click **OK**. Use the mouse wheel to enlarge the retained strip.



IDENTIFY THE ALTERNATING CATION PLANES

Orange = Mg · Blue = Al · Red = O



The lower gap contains **one Al plane**.

The next gap contains **Mg–Al–Mg**, a tetrahedral–octahedral–tetrahedral sandwich.

Count each plane separately. Atoms at different depths overlap in this side view.

↑ [111]
Up: layer stacking

→ [1 1 −2]
Right: along a layer

View along [1 −1 0]
(111) oxygen layers seen edge-on

PREPARE TO COUNT ONE PLANE

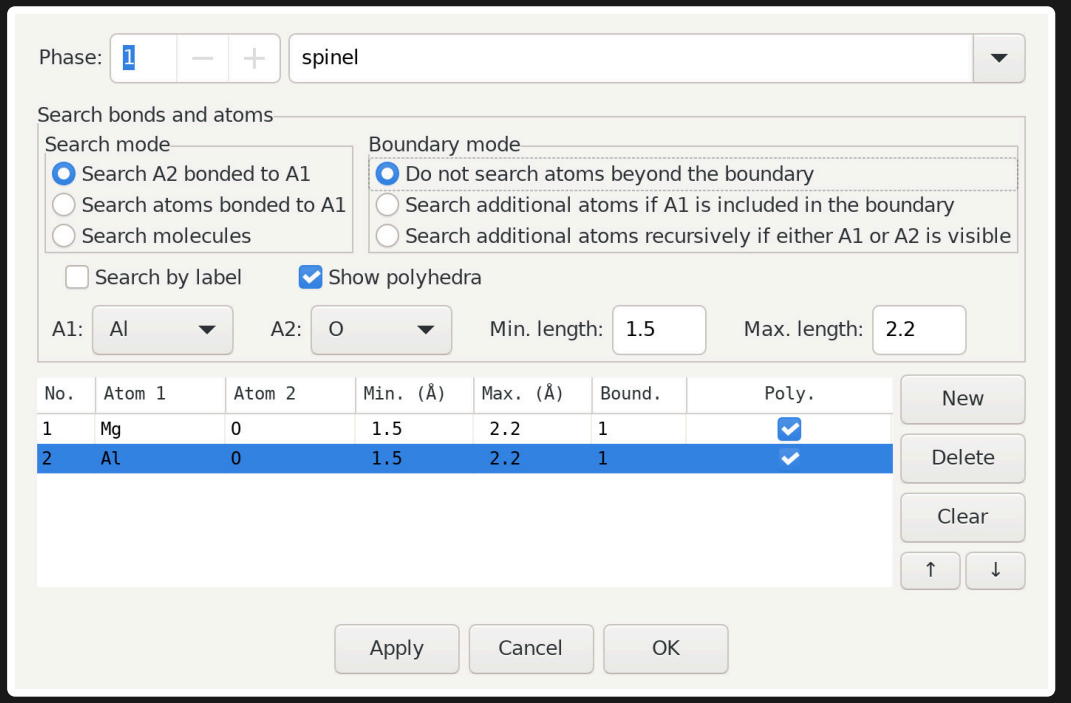
Open **Edit → Bonds…**.

For **both Mg–O and Al–O**, change Boundary mode to **Do not search atoms beyond the boundary**.

Keep **Ball-and-stick** selected.

In **Orientation…**, set projection to **1, 1, 1** and upward to **0, 1, 0**.

We now look straight at an isolated (111) plane.



COUNT THE AL-ONLY PLANE

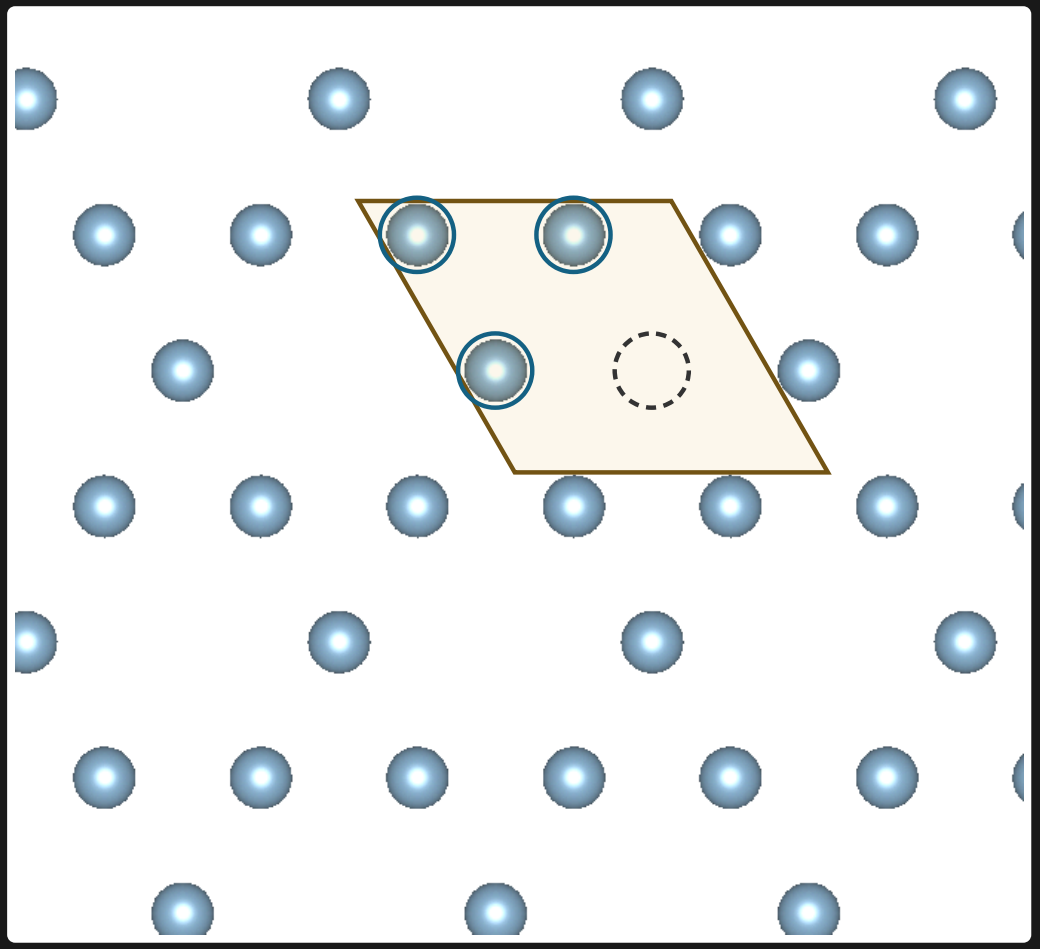
In **Boundary**, select each cutoff row and change its **× d** value:

Plane	× d
(1, 1, 1)	1.40
(−1, −1, −1)	−1.35

The marked repeat contains **four octahedral sites**: three have Al; one is empty.

Al-only plane: ¾ filled.

Solid rings mark occupied sites. The dashed ring marks an empty hole; it is an annotation, not an atom.



COUNT AL IN THE SANDWICH

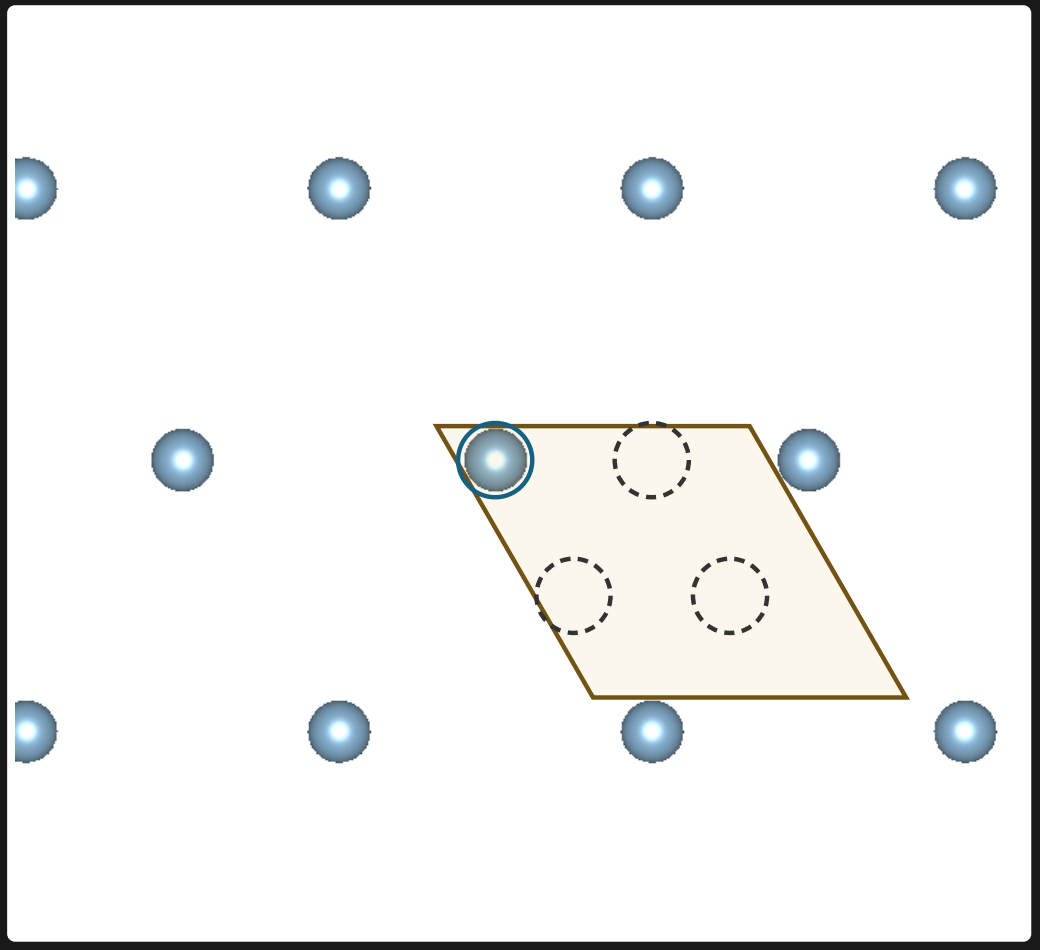
Keep the face-on view and change only the two cutoff distances.

Plane	× d
(1, 1, 1)	1.90
(−1, −1, −1)	−1.85

Now the four-site repeat contains **one Al atom and three empty octahedral holes**.

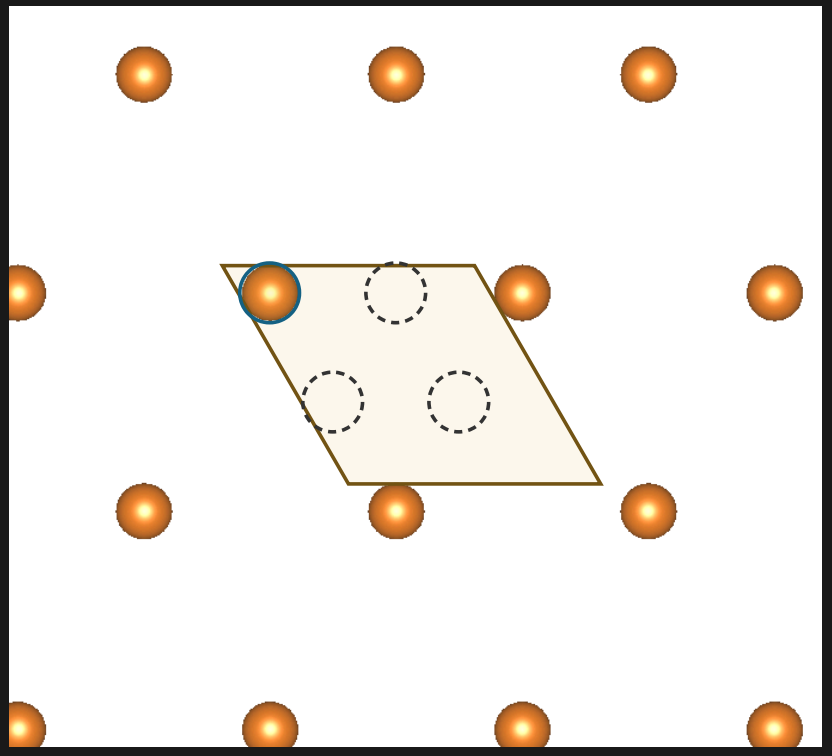
Sandwich Al plane: ¼ filled.

Together, the two Al planes average **(¾ + ¼)/2 = ½**.

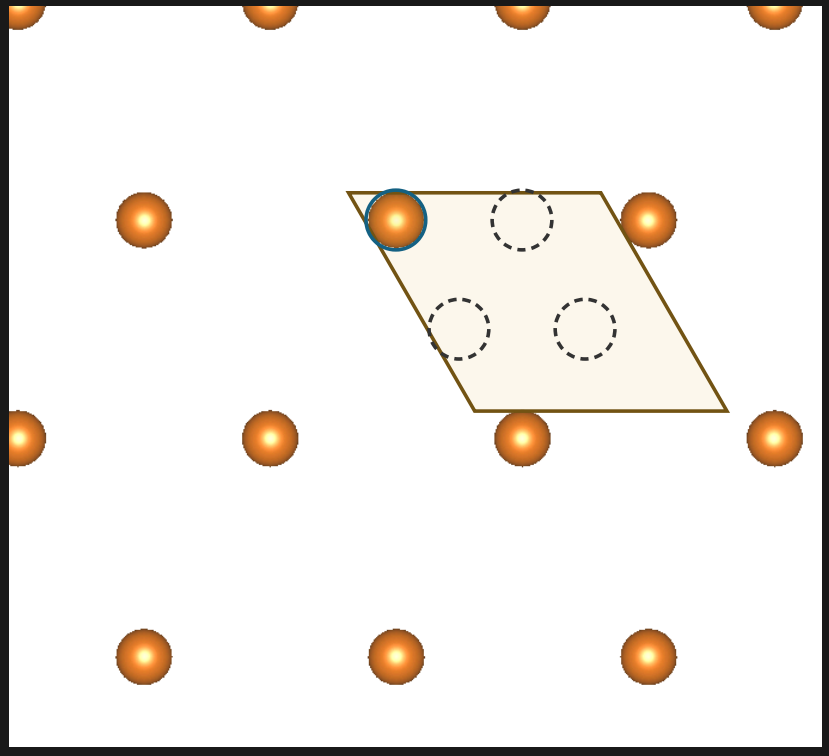


COUNT BOTH MG PLANES

Lower Mg plane: **+1.77 / −1.73**



Upper Mg plane: **+2.02 / −1.98**



Each pair gives the **(111)** / **(−1 −1 −1)** cutoff distances in the **× d** fields.

Each Mg plane fills ¼ of its tetrahedral sites. The alternating Al-only gap has **no Mg**.

PROBLEM 1.31: CHECK THE COMPLETE SOLUTION

Between close-packed oxygen layers, repeat:

Al-only gap	¾-filled octahedral plane
Mg–Al–Mg gap	¼ tetrahedral · ¼ octahedral · ¼ tetrahedral

Hole type	From the planes	From $MgAl_2O_4$
Octahedral	(¾ + ¼)/2 = ½	2 cations / 4 holes
Tetrahedral	(¼ + 0)/2 = ⅛	1 cation / 8 holes

The empty holes are part of **ideal spinel**. In the next lecture, we will describe defects relative to its expected site occupations.

SSMC, Problem 1.31; Lecture 7 VESTA tutorial. Views reproduced in VESTA 3.5.8.

PRACTICE QUESTIONS

Work the Lecture 7 practice questions before the next class. They cover the spinel and garnet structures, cation site preferences, the perovskite framework, and the Goldschmidt tolerance factor.

Open the Lecture 7 practice questions

Every question carries a worked explanation, so you can check your reasoning as you go.