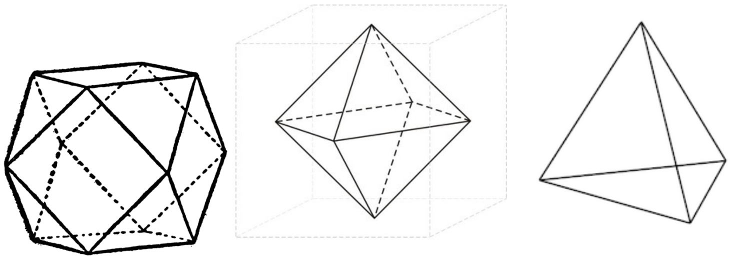
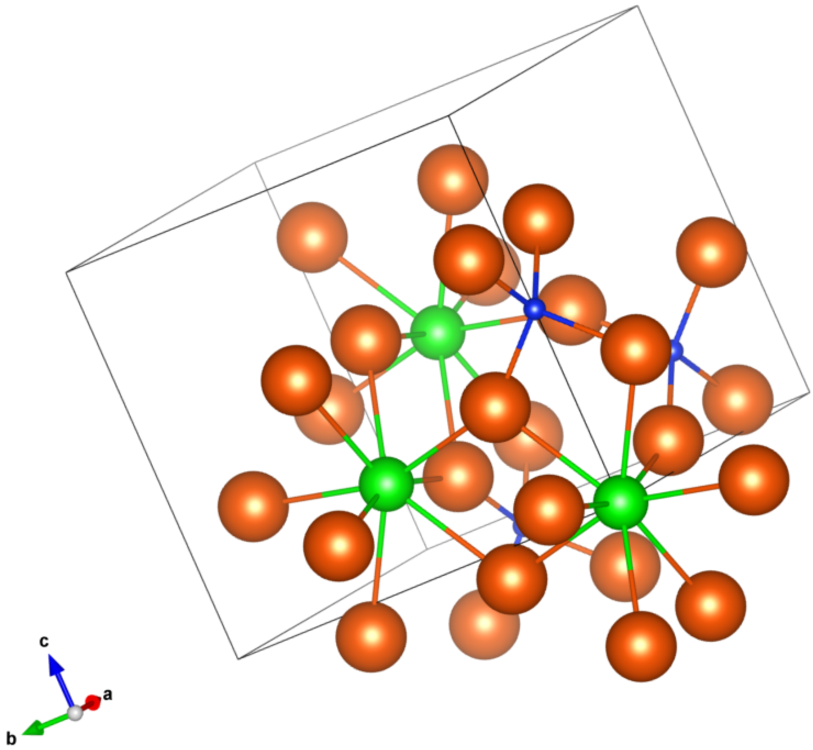
Exercises 2a **25.02.2025**

1. Which of the following objects describes Ti-O and which Ba-O coordination polyhedron in $BaTiO_3$?:



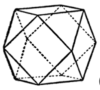
2. Apply Pauling rules to determine coordination numbers (CN) for all ions (cations with respect to the anion and the anion with respect to cations) in $ZrSiO_4$. Based on those CNs, can you identify ions in the picture below, which represents part of the $ZrSiO_4$ structure? The lines connecting the ions present bonds to the nearest neighbors.
Indication: r_{Zr}/r_O =0.68 which is close to the limit of eightfold coordination – so assume eightfold coordination in your analysis

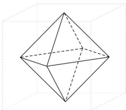


3. Taking $A_a^{CN(A)}B_b^{CN(B)}X_x^{CN(X)}$ where X is an anion, and A and B are cations, verify that $aCN(A) + bCN(B) = xCN(X)$ holds for $ZrSiO_4$.

Solutions:

1. Which of the following objects describe Ti-O and which Ba-O coordination polyhedron?:

Cuboctahedron  describes polyhedron of O around Ba and octahedron



describes polyhedron of O around Ti.

2. Apply Pauling rules to determine coordination numbers (CN) for all ions (cations with respect to the anion and the anion with respect to cations) in $ZrSiO_4$. Based on those CNs, can you identify ions in the picture below, which represents part of the $ZrSiO_4$ structure? The lines connecting the ions present bonds to the nearest neighbors.
Indication: r_{Zr}/r_O =0.68 which is close to the limit of eightfold coordination – so assume eightfold coordination in your analysis

We apply the same method as during lectures for $BaTiO_3$. For $ZrSiO_4$ we have:

r_{Zr}=0.86
r_O=1.26
r_{Si}=0.4

From the Pauling first rule we have:
For Zr, we will assume eightfold coordination. CN(Zr)= 8.

Si is tetravalent, and the coordination in environment of oxygen is most likely tetrahedral. Indeed, r_{Si}/r_O =0.32. Therefore, we take that the coordination number of Si is CN(Si)= 4.

We now need to find coordination number of oxygen, CN(O).
For this we use Pauling second rule:
$CN(O)_{Zr}$*(Bond strength around Zr)+ $CN(O)_{Si}$*(Bond strength around Zr)=absolute value of charge of oxygen.

We first find the two bond strengths:
For Zr: Bond strength around Zr=(valence of Zr)/CN(Zr)=4/8=1/2
For Si: Bond strength around Si=(valence of Si)/CN(Si)=4/4=1

We get:
$CN(O)_{Zr}$ *(Bond strength around Zr)+ $CN(O)_{Si}$*(Bond strength around Si)=absolute value of charge of oxygen --->

$$CN(O)_{Zr} *(1/2)+ CN(O)_{Si}*(1)=2$$

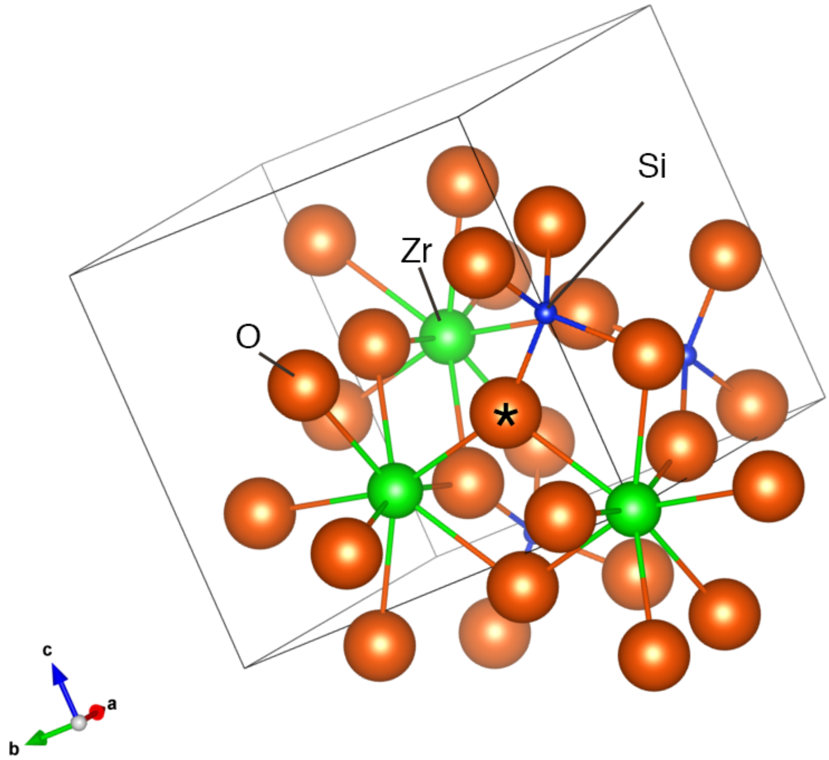
This gives: $CN(O)_{Zr}$ =2, $CN(O)_{Si}$=1

Therefore, each O anion is linked to 2 Zr ions, and 1 Si ion. We write:

$$Zr^{VIII}Si^{IV}O_4^{I+II} \rightarrow Zr^{VIII}Si^{IV}O_4^{III}$$

(if you find more than one solution you may use the method described in problem no. 3 below to verify your choice. You may also think for other physical reasons why one choice is correct).

Representative ions are marked in the picture below. The O ion marked with the star shows that O ions are linked to two Zr and one Si ion, as calculated above. All other O ions have the same coordination but only some atoms and bonds are shown in the picture.



3. Taking $A_a^{CN(A)}B_b^{CN(B)}X_x^{CN(X)}$ where X is an anion, and A and B are cations, verify that $aCN(A) + bCN(B) = xCN(X)$ holds in 1) and 2).

For $Zr^{VIII}Si^{IV}O_4^{III}$ → 1*8+1*4=4*3