



5.1 Even More Structure



LEARNING GOALS

Learning Objectives

1. Perform calculations involving the theoretical density of a ceramics having the CsCl or ZnS crystal structures
2. Explain the arrangement of anions and cations in the CsCl or ZnS crystal structures
3. Demonstrate the cation and anion coordination number and coordination geometry (interstitial site) for the CsCl or ZnS crystal structures
4. Show how both octahedral and tetrahedral interstitial sites exist between planes of close-packed atoms

A Seemingly Familiar Ceramic Crystal Structure - CsCl

For this section, I'd like to try something new and show you the structure first, and then explore and describe its attributes. Figure 1 shows the CsCl ceramic crystal structure.

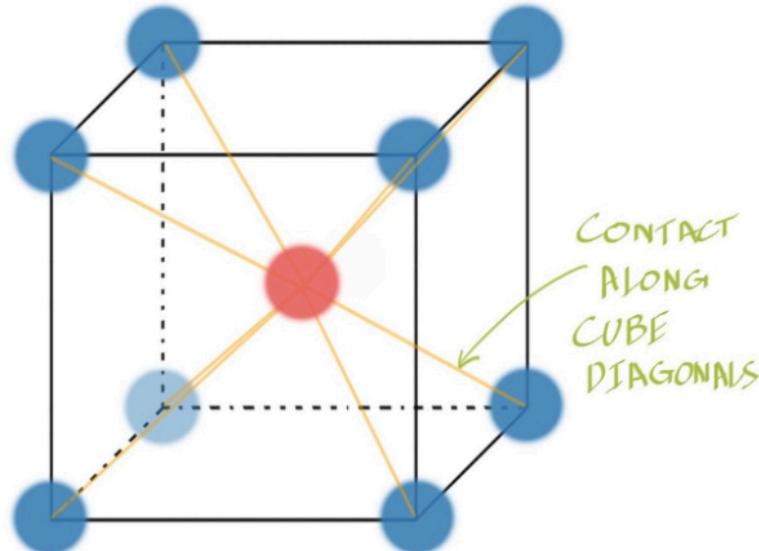


Figure 1. The cesium chloride (CsCl) ceramic crystal structure. The anions are arranged in a simple cubic lattice, with cations occupying the simple cubic interstitial sites.

It is likely that it looks familiar. At first glance, you are likely to ask, "how is this different from the BCC crystal structure?" This is actually a very good question to ask and it shows that you are making

connections between different parts of this course. It also shows that you are quite familiar with the metallic crystal structures. Yes, CsCl does look very similar to BCC, in fact, the atom positions are essentially the same. The only distinction, and this is an important one, is that CsCl represents structures having two atom types: an anion and a cation, while BCC represents a structure in which there is only one atom type. Of course, from this distinction it then becomes clear that the APF and density will require different calculations, and the relationship between the lattice parameter and the atomic radii must be different. You'll recall that for BCC, $a = \frac{4}{\sqrt{3}}R$, however for CsCl the full cube diagonal would equal $2R_A + 2R_C$.

Double Checking the Stoichiometry

It's always worthwhile to double check the stoichiometry, as we did for NaCl to discover that we needed a cation at the centre of the unit cell. The stoichiometry in CsCl is 1:1 and the unit cell has 8 anions in corner positions, each contributing $\frac{1}{8}$ of an atom for a total of 1 anion. There is one complete cation at the centre of the unit cell, not cut up. This gives one anion and one cation, so we are feeling pretty good about ourselves.



The Coordination Number for Cations in CsCl

If you recognized the similarities between CsCl and BCC it shouldn't be a surprise that the coordination number of the cations in CsCl is eight. The cation, located at the centre of the unit cell is equidistant from each of the eight corners and makes contact with each of them.

Cation Coordination Number_{CsCl} = 8

A Little Twist on Something Familiar - ZnS

For this section, let's build up the ZnS crystal structure together, as we did for NaCl. First, we start with anions in "FCC-type" positions, as in Figure 2.

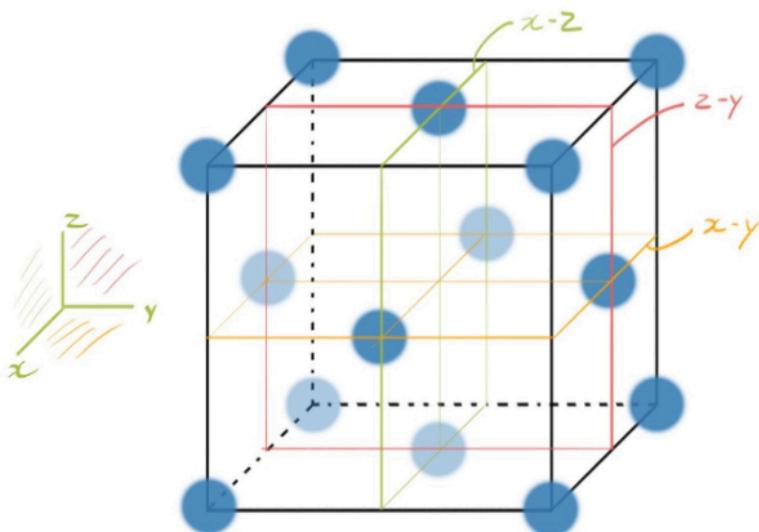


Figure 2. The ZnS ceramic crystal structure can be described beginning with an FCC lattice of anions. Cations will go into interstitial sites within this lattice and the unit cell has been sliced into 8 "sub-cubes" to help visualize these interstitial sites in a moment.

You will, of course, notice that Figure 2 also has a number of lines drawn on it that are not typically there. What I have done is sliced the unit cell in half in three planes, the x-z plane, the z-y plane, and the x-y plane. This yields eight smaller cubes, sometimes I call them *sub-cubes*.

These sub-cubes are useful in understanding the ZnS ceramic crystal structure since at the very centre of each of these lies a *tetrahedral* interstitial site. One of these interstitial sites is illustrated in Figure 3.

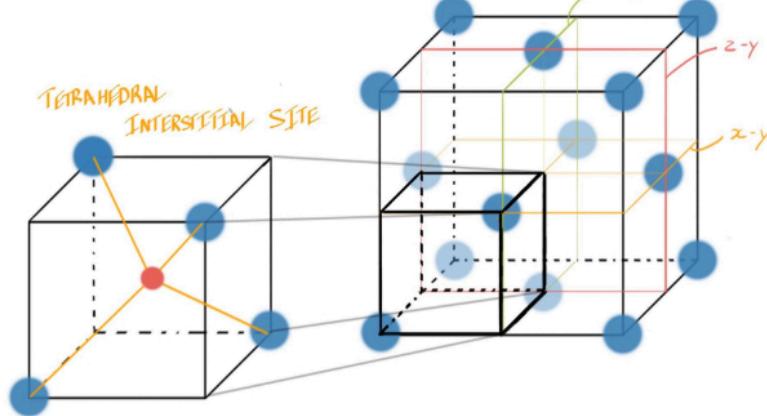
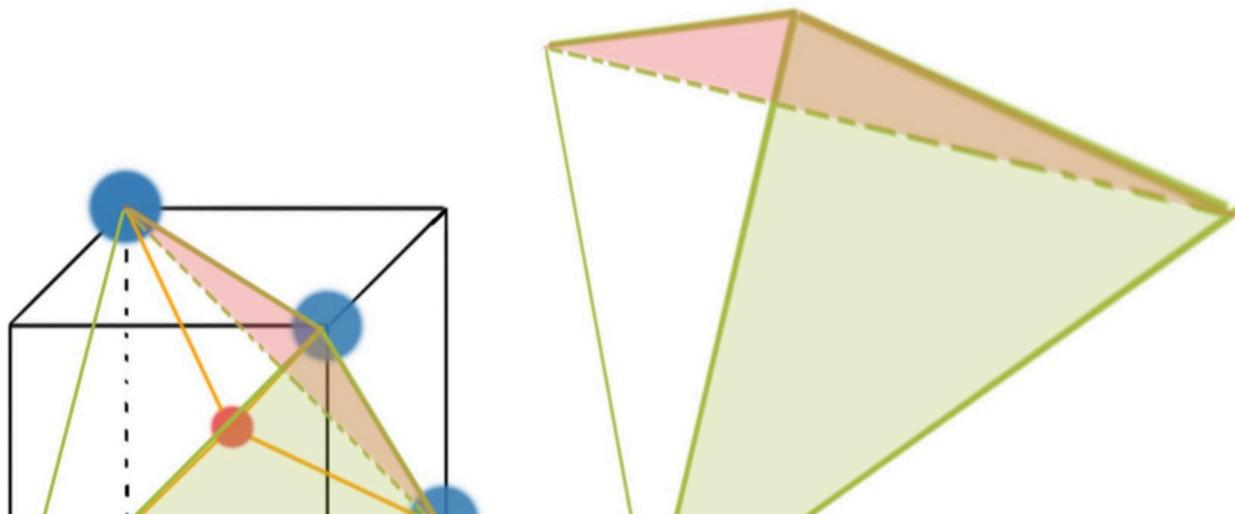


Figure 3. The tetrahedral interstitial site can be visualized as the centre of one of these sub-cubes. A cation occupying one of these sites would have a coordination number of 4.

The tetrahedral interstitial site has a coordination number of four. That is, an atom located in the centre of this site would touch four nearest neighbour atoms. However, please remember that interstitial sites are named according to the solid geometry that they create, not their coordination number. I mention this now, because often the tetrahedral interstitial site creates confusion because it has a coordination number of four and also creates a four sided solid - the tetrahedron. I have illustrated a tetrahedral interstitial site in Figure 4.



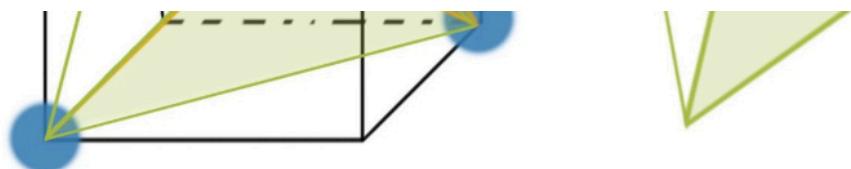


Figure 4. The tetrahedral interstitial site is so-named because it creates a four sided solid. In this illustration I have shaded in a couple of the faces to help visualize this geometric solid. In the tetrahedron drawn outside of the cube I also rotated it a little in the hopes that the perspective would be easier to visualize.

Double Checking the Stoichiometry

You may be surprised that I have suddenly jumped to checking the stoichiometry without first completing the ZnS structure. I did this on purpose because I'm hoping that you have identified a problem with what I have described so far. We have divided the unit cell into eight sub-cubes and have described a tetrahedral interstitial site at the centre of each, however, this would give us 8 cations, while the FCC lattice of anions gives us only 4 anions. So, the answer to this is that only half of the available tetrahedral interstitial sites are occupied. Don't fall into the common conceptual trap of believing that every interstitial site somehow must be occupied. An interstitial site is just a potential space where an atom could be located.

So, now we are ready to look at the complete ZnS ceramic crystal structure!

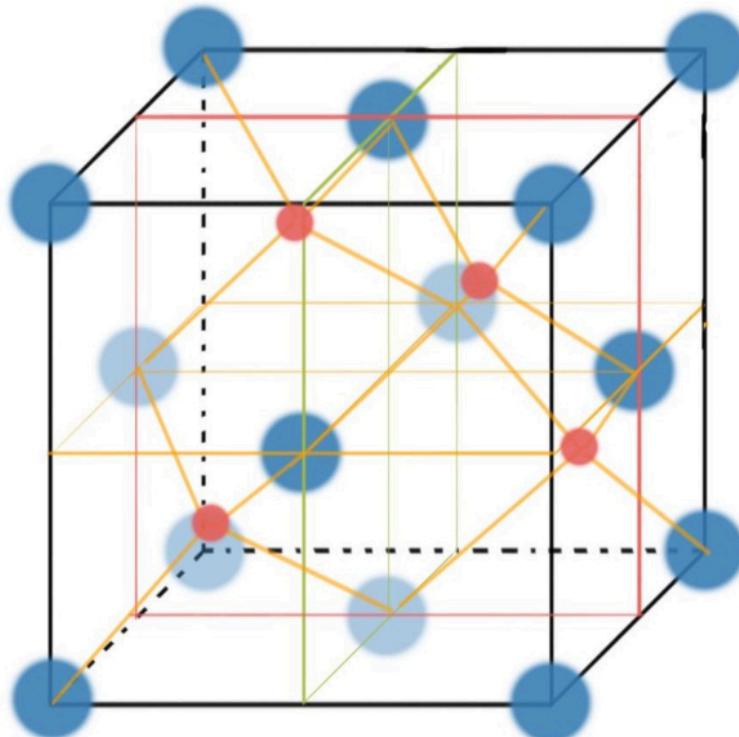


Figure 4. The complete ZnS ceramic crystal structure. I have drawn in the orange lines showing the direction of contact between cations and nearest neighbour anions.

Since only half of the sites will be filled, it would not make sense for all of the interstitial sites, say, at the bottom of the unit cell to be occupied. There is charge repulsion between like charges and so they

will distribute themselves as far apart from one another as possible. This is illustrated in Figure 4.

Sometimes, with all of the orange lines drawn, it is difficult to visualize the positions of the occupied interstitial sites. Several years ago a student showed me a technique that helped her to understand these positions.

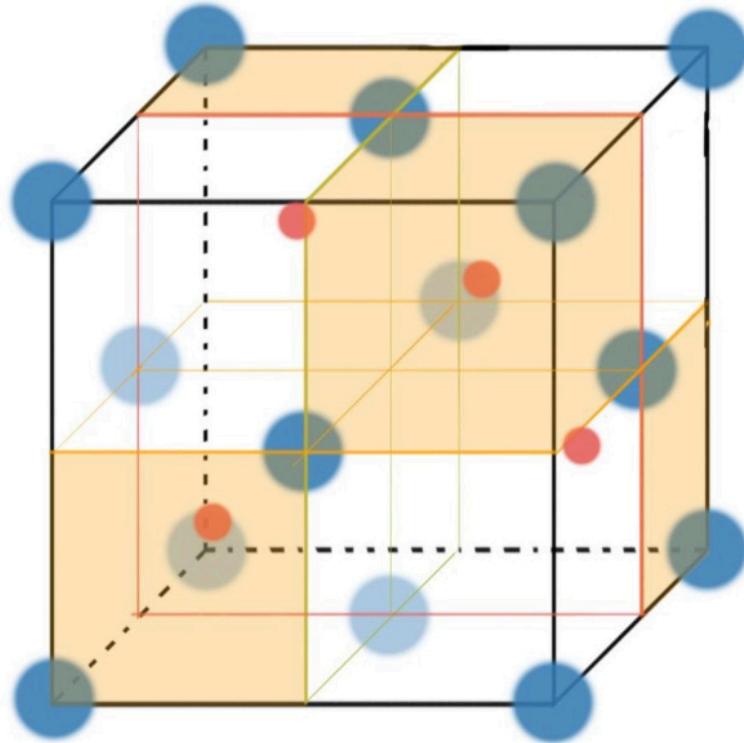


Figure 5. The complete ZnS ceramic crystal structure with the exposed surfaces of the occupied tetrahedral interstitial sites shaded.

She shaded in the exposed faces of the sub-cubes containing occupied tetrahedral interstitial sites. I think this is a really nice way to look at this structure so I have re-drawn the ZnS structure in this manner in Figure 5.

The Coordination Number for Cations in ZnS

Well, after all this talk about the coordination number of the tetrahedral interstitial site, I hope that it will be fairly clear that each cation is coordinated with 4 anions.

Cation Coordination Number_{Zinc Sulphide} = 4

How About Something With a New Stoichiometric Ratio? Calcium Fluorite, CaF₂

So far we have seen only ceramic crystal structures with a 1:1 stoichiometric ratio of anions to cations.

How about something new?

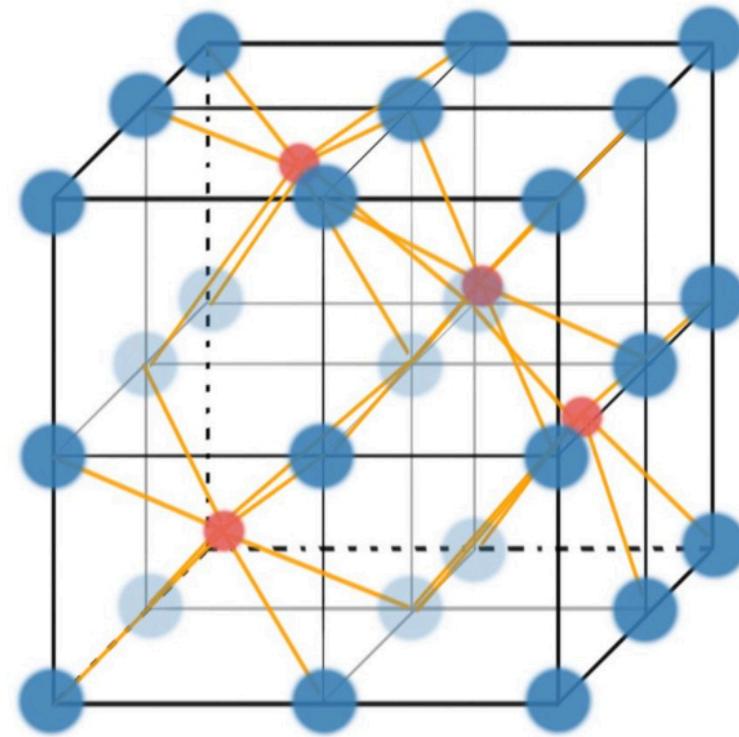
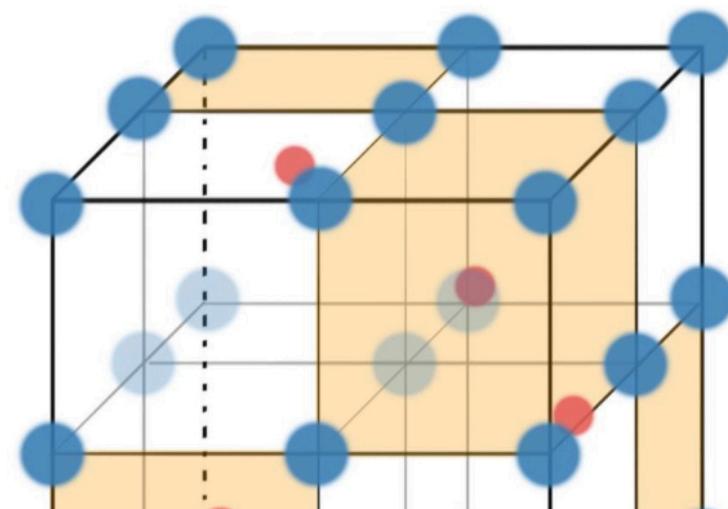


Figure 6. The calcium fluorite ceramic crystal structure. Anions represented as blue dots are in a simple cubic lattice with half of the simple cubic interstitial sites occupied by cations. Cations touch their 8 nearest neighbour anions along the cube diagonals, as illustrated by the orange lines.

What's more new and fresh than calcium fluorite? Let's start with the size of the cations relative to the anions. They are quite large; in fact, the cations occupy the largest of our three interstitial sites: the simple cubic site. Now, you may well recall that CsCl had cations occupying the simple cubic interstitial sites, and you are correct. Of course, the difference lies in the stoichiometry. While CsCl had an equal number of anions and cations, CaF₂ has twice as many anions as cations. This is achieved in a similar manner to the structure of ZnS. That is, only half of the available interstitial sites are occupied. This is illustrated in Figure 6 and Figure 7.



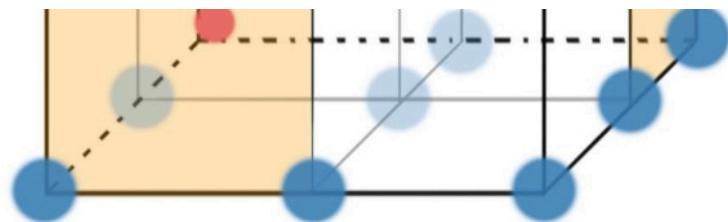


Figure 7. The calcium fluorite ceramic crystal structure with occupied simple cubic interstitial sites identified with orange shading on the exposed surfaces of the populated sub-cubes.

With all of the coordination directions identified, as they are in Figure 6 the sketch gets very messy and it may be difficult to make sense of what you are looking at.

Figure 7 attempts to ease this mess by shading in the exposed faces of the sub-cubes containing occupied simple cubic interstitial sites.

Double Checking the Stoichiometry

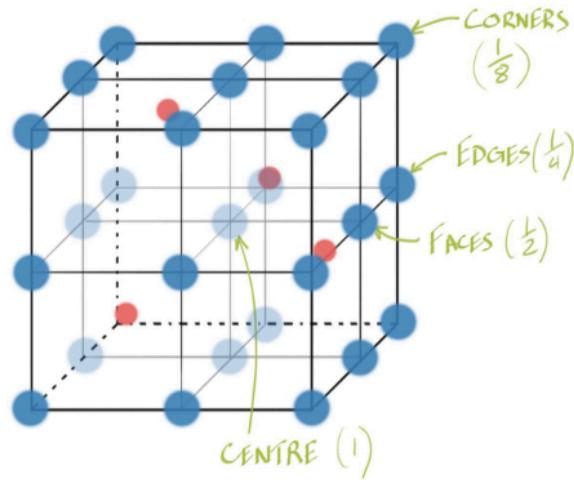


Figure 8. There are 8 anions within the calcium fluorite ceramic crystal structure. The fraction of an atom for each position type is shown here.

It's always good practice to double check our stoichiometry, so let's do that now.

The cations are fairly straight forward since they are located completely within the unit cell. There are four cations. The anions take a little more work and I have illustrated it in partially in Figure 8. There are eight corners, six faces, twelve edges, and one central anion.

$$\frac{1}{8}8_{(\text{Corners})} + \frac{1}{2}6_{(\text{Faces})} + \frac{1}{4}12_{(\text{Edges})} + 1_{(\text{Centre})} = 8$$

All The Interstitial Sites (That We've Seen)

So far, we have seen three types of interstitial site. They are, in increasing size order: tetrahedral, octahedral, and simple cubic. A cation in a ceramic crystal structure will not occupy an interstitial site in which the cation cannot touch the nearest neighbour anions. Typically, in fact, the cation pushes the anions apart so that the cation is touching the nearest neighbour anions and the anions are not touching one another.

Tetrahedral and Octahedral Interstitial Sites Between Close Packed Planes

Now that you're well on your way to becoming a veritable expert on octahedral and tetrahedral interstitial sites, let's take a look at another way of understanding them.

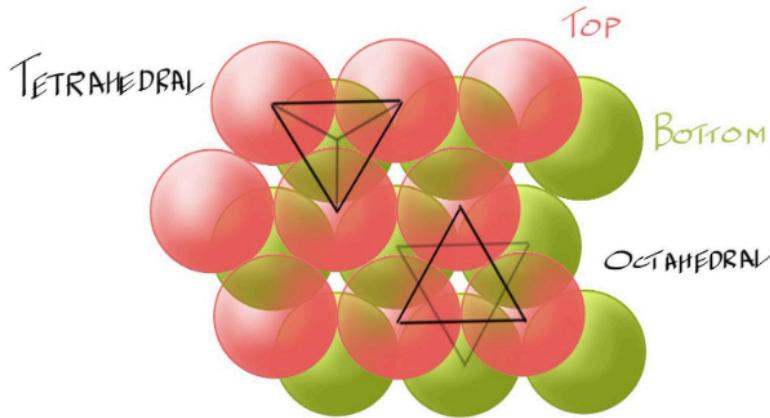


Figure 9. Anytime we stack two close-packed planes tightly on one another, as we do in both FCC and HCP structures, we create both tetrahedral and octahedral interstitial site

Any time that we stack two close-packed planes we actually create both octahedral and tetrahedral interstitial sites, as shown in Figure 9. If you look normal to the close-packed planes and peek through the space between three touching atoms you will either see an atom below (green atoms in the figure) or you will see the white color, having peeked also through the green atoms. When you see the green atom between the three red atoms you are looking into a tetrahedral interstitial site, located exactly in the middle of the red and green planes. This is because you see a site surrounded by four atoms, or a coordination number of 4. On the other hand, if you see the white colour between the red atoms this means that you are looking through both the top and bottom planes and into a space with a coordination number of six - an octahedral interstitial site.