# 5.2 Calcium Fluorite

LEARNING GOALS

## Learning Objectives

1. Perform calculations involving the theoretical density of a ceramics having the $CaF_2$ crystal structure
2. Explain the arrangement of anions and cations in the $CaF_2$ crystal structure
3. Demonstrate the cation and anion coordination number and coordination geometry (interstitial site) for the $CaF_2$ crystal structure

## How About Something With a New Stoichiometric Ratio? Calcium Fluorite, $CaF_2$

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

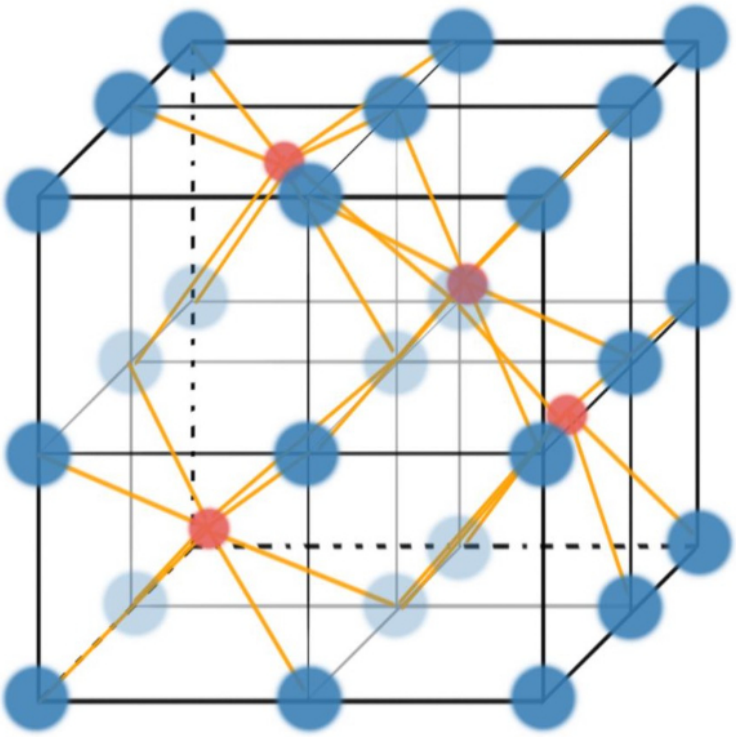

**Figure 6.** The calcium fluorite ceramic crystal structure. Anions represented as blue dots are in a simple cubic lattice with half of the simple cubic interstitial

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, $CaF_2$ 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.

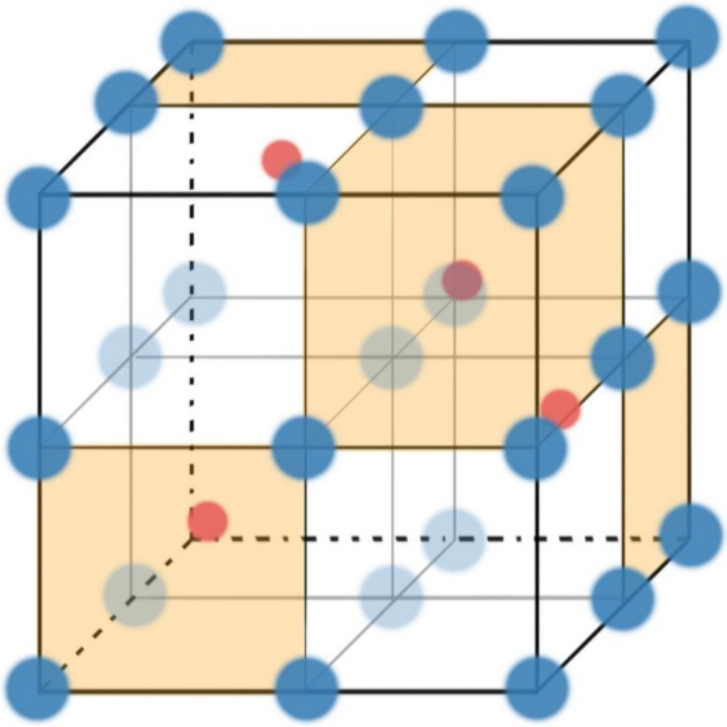

**Figure 7.** The calcium fluorite ceramic crystal structure with occupied simple cubic interstitial sites identified with orange shading on the exposed surfaces of the populated sub-cubes.

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

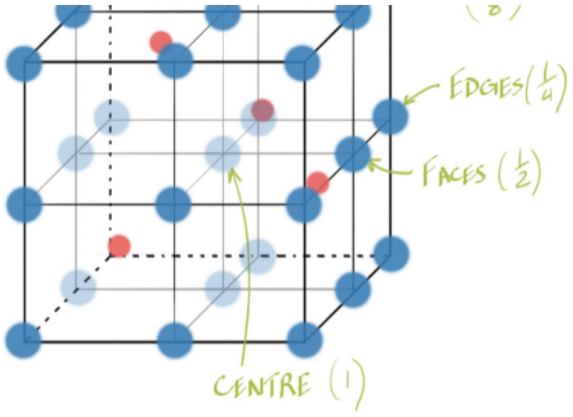


**Figure 8.** There are 8 anions within the calcium fluorite ceramic crystal structure. The fraction of an atom for each position type is shown here.

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.

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

## The Coordination Number for Cations in $CaF_2$

You guessed it. The coordination number for cations in calcium fluorite is 8.

$$\text{Cation Coordination Number}_{Calcium\ Fluorite} = 8$$