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Question 1
Briefly explain the two key factors that determine the crystal structures of ceramic materials. Discuss why NaCl has the following crystal structure. [**10%**]

The two key factors which determine the crystal structures of ceramic materials are:

1. **The magnitude of the electrical charge on each of the component ions.** Most crystals are composed of a metal and a non-metal, which, after losing and gaining electrons, become cations and anions respectively. These crystals (with some exceptions) must maintain *electrical neutrality* (a net charge of 0), and so cations and anions must combine in different ratios to ensure this. It is this ratio which plays a major part in determining the crystal structure of the ceramic.

2. Every cation and anion prefers to have as many nearest-neighbour ions of the opposite charge surrounding them, as this is when stable ceramic crystal structures can form. The maximum number of oppositely-charged neighbouring ions is known as the *coordination number*, and is intrinsically based on **the relative sizes of the cations and anions.** Hence, for each coordination number, there is a critical value for the ratio of cation to anion size r_c/r_a for which this condition is met.
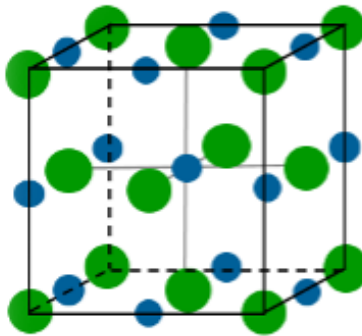

Figure 1: The crystal structure of NaCl.

Question 2

ZnS is of the following crystal structure. Explain why only a half of the tetrahedral interstitial positions are occupied by Zn^{2+}. **[10%]**

ZnS is of zinc blende structure (also known as *sphalerite*) which has a coordination number of 4 and thus has a tetrahedral shape. In essence, the zinc blende structure is where all corner and face positions of the cubic cell are occupied by anions, while cations fill interior tetrahedral positions. However, as the question notes, only half of the possible 8 tetrahedral interstitial positions are filled by the Zn_2^+ cations. This is due to two reasons: (1) to separate the like charges (cations) maximally in space, and, perhaps more importantly, (2) to maintain stoichiometry. Note that the anions are essentially positioned in an FCC structure. Therefore, the total number of anions n_a that count towards the electrical charge for one unit cell is

$$n_a = 8 \text{ corner atoms} + 6 \text{ face atoms} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4. \tag{1}$$

Hence the anions provide a total charge of 4− to the crystal. In order to balance this out to maintain electroneutrality, only 4 cations (each providing a charge of 1+) are required, and hence only a half of the 8 total tetrahedral interstitial positions are required to be filled.
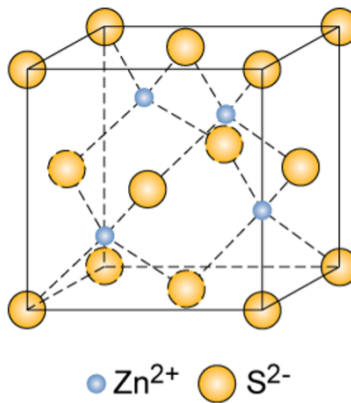

Zn^{2+}　　S^{2-}

Figure 2: The crystal structure of ZnS.

Question 3

List the names of at least 5 forms of carbon structures. **[5%]**

5 forms of carbon structures are:

1. Amorphous carbon/carbon black

2. Tetrahedral diamond cubic

3. Graphite

4. Graphene

5. Fullerenes and carbon nanotubes

> **Question 4**
>
> In potassium oxide (K_2O), the ionic radii of K^+ and O^{2-} are 0.138 nm and 0.140 nm, respectively. **[25%]**
>
> a) What would be the coordination number for each O^{2-} ion? **[5%]**
>
> b) What would be the crystal structure of K_2O? **[10%]**
>
> c) If MgO is added as an impurity in K_2O, what point defects are possible to maintain charge neutrality? **[10%]**

Table 12.2: Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios (r_C/r_A)

Coordination Number	Cation-Anion Radius Ratio	Coordination Geometry
2	Less than 0.155	Linear
3	0.155 - 0.225	Triangular
4	0.225 - 0.414	Tetrahedral
6	0.414 - 0.732	Orthorombic
8	0.732 - 1.0	Cubic

a) Consider the ratio of the ionic radii of K^+ and O^{2-}:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.138}{0.140} = 0.9857... \approx 0.99 \tag{2}$$

The cation-anion radius ratio is approximately 0.99. According to Table 12.2 from CALLISTER 2018, this associates to a coordination number of 8.

b) The crystal structure/coordination geometry associated with a coordination number of 8 is the cubic structure, also known as the CsCl cesium chloride structure. In this structure, anions are at each corner of the cube, with a single cation at the cube centre. Note that one unit cell consists of eight cubes in total. As K_2O contains twice as many cations as anions, only half of the eight cubes forming the unit cell will contain a potassium cation at their centre. A schematic for this structure is shown in Figure 3, where green spheres represent oxygen anions and blue spheres represent potassium cations.
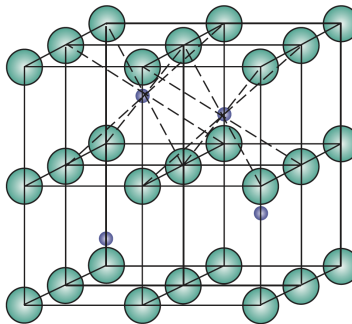

Figure 3: The crystal structure of K_2O.

c) If MgO is added as an impurity in K_2O, the Mg^{2+} cation will replace two K^+ cations. Hence, there will be a cation vacancy in the lattice i.e. a net $1-$ charge. In order to maintain electrical neutrality, an $1-$ charge must be removed from the lattice, or a $1+$ charge must be added to the lattice. As the anion present is oxygen, which has a $2-$ charge, the first option is not possible. Hence the only option is for another K^+ cation to embed itself in the lattice.

> **Question 5**
> Explain (1) why ceramics are much more brittle than metallic materials and (2) why the fracture strength of
> bulk ceramics decreases with increasing specimen size. **[10%]**

(1) Ceramics are much more brittle than metallic materials as plastic deformation is more difficult in ceramic lattices. This is mainly for two reasons:

  i. the dislocation core structure is extremely complex, which makes the motion of the dislocation difficult.

  ii. slippage is incredibly difficult as either the plane is not a close-packed plane, or two ions of the same charge would have to slip past one another causing a repulsive force; overcoming this force would require an incredible amount of energy.

Reduced dislocation motion causes a reduction in the ability for the material to plastically deform, which in turn increases the brittle nature of the material.

(2) Ceramics are not completely dense material — most ceramics have some % porosity, meaning that there are empty gaps (pores) present in the lattice. There are also usually many cracks present as well, which, combined with the voids, act as stress concentration sites. Hence, the more pores and cracks present in the sample, the lower the overall fracture strength. Now, though the % porosity may remain the same, larger specimens will have a higher absolute number of pores as well as longer cracks. Recall that according to the stress concentration relationship (equation 3), the stress concentration factor σ_m/σ_0 is directly proportional to the length of the crack a. Thus both the longer cracks and the greater number of pores will result in larger specimens having lower fracture strengths.

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{\frac{1}{2}} \tag{3}$$

> **Question 6**
> A thick and a thin glassware are heated in an oven simultaneously and cooled in air. Which one is subjected
> to a higher thermal stress? Why? **[10%]**

The magnitude of the thermal stress induced in a material is proportional to the differences in the cooling rates of the exterior and interior of the material. Now, for both thick and thin glassware, the exterior cooling rate is going to be quite similar as they are both placed in the same environment (air). However, due to the thickness having a "shielding" effect, the cooling rate of the interior of the glassware differs with the thickness of the specimen. A thicker specimen has a larger difference across the boundary of the glassware, and so will have larger thermal stresses induced.

> **Question 7**
> Write a short description on the process of slip casting of ceramics. You can watch the YouTube video:
> https://www.youtube.com/watch?v=IdBN9oUM5B4 for this question. **[15%]**

There are essentially 6 steps to the process of slip casting ceramics.

1. **Clean the mould.** The moulds are made of a hard white substance created by the addition of water to powdered and partly dehydrated gypsum, generally known as *Plaster of Paris*. They are quite fragile. The first step is to clean the mould, checking for any damage, leftover clay, or dust particles, as these can all have an undesired effect on the final product.

2. **Close and strap the mould.** The mould is made up of two separate halves designed to fit together. It is necessary to find a tight way to keep the two sides of the mould together, so either use multiple different sized rubber bands or a universal mould strap.

3. **Pour the slip and wait.** Once the two halves of the mould are strapped together, they are ready to have liquid clay (slip) poured into the negative space created by the mould. Pour the casting slip through the opening of the mould. Fill the mould all the way, past the brim, up until the rim. The Plaster of Paris will absorb some of the moisture from the slip, and a skin will start to form on the inside of the mould. The thickness of the skin will depend on how long you let the slip sit.

4. **Drain and wait.** Once the skin starts to form, you want to pour the excess slip out of the mould. You will see the skin of the clay on the inside which has now begun to form according to the desired shape. Let the slip now air dry. After a while, you will notice that the slip starts to pull away from the mould as the moisture has evaporated and the clay has shrunk.

5. **Remove from mould.** Trim out the excess, and then remove the first half of the mould. The clay is currently still extremely fragile, but a solid shape should be formed in the shape of the mould.

6. **Fettling.** Trim and shave the excess or the seam off the clay using a clean-up tool. Use a sponge to blend any blemishes off the surface of the cast.

Question 8
Watch the following YouTube video and write a short description on how sheet glass can be produced: https://www.youtube.com/watch?v=IjNusHQOhTM. [**15%**]

The key elements to sheet glass besides sand are soda ash (Na_2CO_3), and lime ($CaCO_3$). These two chemicals lower the melting point of silica sand and alter its basic molecular structure (terminating the $Si-O$ chains).

Once these compounds have all been mixed, they are placed into tanks which are kept at approximately $1650°C$. The mixture is manually raked to reduce air pockets which might have pooled up, resulting in liquid glass. This mixture is superheated for ten hours to allow any gas to bubble up and out, preventing air bubbles in the final product.

Now, to ensure the final product is a flat sheet of glass, the molten glass is poured over a bed of liquid tin. Tin and glass do not mix; the lighter glass floats on the denser tin. Tin also has a lower melting point. Hence, after the molten glass is poured onto the molten tin, the mixture is cooled on a long conveyor-belt-esk system where, by the end, the glass is a solid flat slab and the tin is still molten. At this point, the glass slab is about 400m long. A robot then cuts the glass into smaller sheets, resulting in sheet glass.