Chemistry in Crystallography

I recently took the Beauty of Symmetry course. The course included a section of crystallography, where I will now explore its chemistry. The idea came from the Learning Log's Week 6 question "Crystals can be strikingly beautiful. Describe the external form of your favorite crystal". Some peers' answers:

Fatehah \rightarrow **Tanzanite** has a beautiful shade of blue, which makes it special and unique. It's shining and sparkling.

Santhiya \rightarrow **Quartz**. The trigonal bipyramid form has triangles and forms rhombs.

Jesselyn \rightarrow **Diamond** has a symmetrical octahedron shape which looks like two four-sided pyramids placed base to base, which makes it simple yet beautiful.

 $Me \rightarrow The$ **bismuth** crystal is particularly beautiful. While it has a rhombohedral structure, these crystals tend to have a rectangular, spiral 'hoppered' shape as they have higher growth rates on the outside edges. Bismuth crystals are highly vibrant in colour. This is due to an uneven layer of bismuth oxide on the crystal's surface which causes different wavelengths of light to reflect constructively at different points, hence the different colours.



Crystals can be very beautiful indeed. This is because of how the atoms are arranged within them which gives them their shapes and often their highly vibrant colour(s).

Their creation generally starts with a phase called nucleation.¹ The first part is primary nucleation, where a new crystal is formed. It happens when a few of the ions/atoms/molecules arrange themselves in the pattern characteristic of a crystalline solid.² Having a supersaturated solution (one where there is more solvent than what can be dissolved in the available solute) will allow nucleation to take place via the undissolved solvent, making it easier to get through the primary nucleation phase as the 'seeds' would have been provided. The second part is secondary nucleation, where crystal growth from the 'seed' is initiated with contact and crystal growth at this point is optimized at a lower supersaturation.³ There are both homogeneous and heterogeneous forms of nucleation; heterogeneous means using a speck of dust or some other impurity as a starting point, while homogeneous would involve building directly onto the existing crystal structure (usually more prominent in secondary nucleation).⁴

¹What is a crystal?

² Definition of Nucleation

³ Kinetics of Nucleation

⁴ Primary and Secondary Nucleation

Crystals exhibit different types of bonding depending on its constituent ions/atoms/molecules. Those with non-metals only (e.g. quartz, diamond) form giant covalent structures. Those with both metals and non-metals (particularly those with large difference in electronegativity values, such as sodium chloride) form giant ionic structures. Metallic crystals will have metallic bonding. They typically have high bonding strength between the constituent particles and hence often have high boiling points. The type and strength of the bonding between each particle also determines how hard it is.

The colours of crystals are determined by its constituent ions/atoms/molecules. If you noticed, the crystals without transition metals tend to be colourless/white, while those with a transition metal would have colour. This is due to a property of transition metalss when there are other polar molecules/ions nearby where the energy of their d orbitals get perturbed by different amounts depending on their position relative to the charged particles nearby. For those which have partially filled d orbitals, the electrons can jump between the higher and lower energy levels of the d orbitals, absorbing a particular wavelength of energy in the visible region and reradiating it in a random direction. It causes our eyes to perceive its colour as the sum of the rest of the wavelengths, giving the crystal its colour.

Bismuth, however, gets its colour from an uneven coating of bismuth oxide on its surface, causing different wavelengths of light to reflect constructively at each point and giving each point a different colour.⁵

Some crystals have allotropes, which mean that they can have different arrangement of their constituent particles depending on which form is the most thermodynamically favourable for a given combination of temperature and pressure. These can be represented by phase diagrams. Carbon, for example, can take the form of carbon nanotubes, diamond, graphite or Buckyballs, among others. Of the macro structures it can form as, it becomes graphite at lower pressures and diamond at higher pressures.⁶ It can even take on a metallic form if pressure is sufficiently high. However, diamonds do not transform into graphite as the activation energy needed for this rearrangement of crystal structure to take place is simply too high and not thermodynamically feasible. Each of these allotropes have unique properties: graphite is good for a lubricant and electrical conductor; diamond for its hardness and carbon nanotube for its strength (space elevators).⁷ Tin is another example, changing its crystal form depending on temperature. At 13 degrees Celsius and above, it takes on a tetragonal structure which is highly malleable; however, below that temperature, it changes to a crumbly, grey diamond cubic structure which is brittle. Unlike carbon, however, this activation energy is much lower, which allows this change to take place. Known as tin pest⁸, this is one of the factors that doomed Robert Scott in his Antarctic expedition to the South Pole. He had used tin to store fuel needed to melt water and cook food; however, much of it leaked out due to the change in tin's crystal structure and onto the food supplies, leaving his team without the much needed energy to carry on.



- ⁵ Bismuth Crystal creation
- ⁶ Diamond creation
- Space elevator
- ⁸ Tin pest

Various crystals are obtained from mining them or their ores etc. from underground and possibly from the sea. While some of them are prohibitively expensive (e.g. gold mining from the seas), there are others that are within cost so resources are deployed over extensive areas where the crystals the companies are trying to find are believed to be in. Unfortunately, especially when law enforcement is weak or absent, they destroy the environment in the process of mining the crystals. Whole swaths of land can become uninhabitable as the vegetation and topsoil are removed in search of these ores/crystals. Many species can be forcibly relocated or driven to extinction due to this.

This environmental destruction can lead to economic and social impacts. The immediate economic gain is wiped out by the negative externalities borne by others from such mining activities; this is exacerbated by how the poor tend to be most dependent on their land for their shelter and livelihood (farming) so it increases income inequity...

Questions that I might formulate: Is there a way for tin (or any other allotrope for that manner) to remain in the favourable crystal structure given that it is not in the conditions to naturally do so?

In conclusion, crystallography can be highly beautiful, but it can also contribute significantly to functional uses such as drills and wires. Please do take the next offering of the Beauty of Symmetry course to learn more about the math behind it!

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Bibliography: Tim White (and by extension <u>Fatehah</u>, <u>Santhiya</u> and <u>Jesselyn</u>) for the <u>Learning</u> <u>Logs</u> and the idea itself <u>What is a crystal?</u> <u>Definition of Nucleation</u> <u>Primary and Secondary Nucleation</u> <u>Kinetics of Nucleation</u> <u>Bismuth Crystal creation</u> <u>Diamond creation</u> <u>Tanzanite creation</u> <u>Space elevator</u> Tin pest

