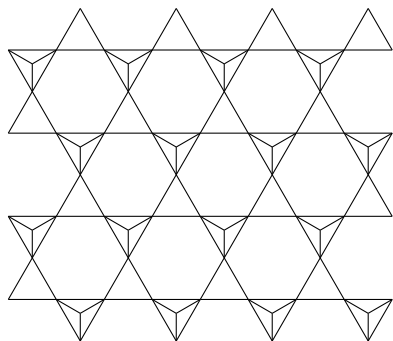
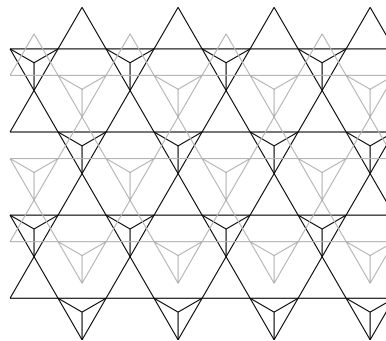


## Lecture Notes - Silica Polymorphs

- Many minerals are known that have the chemical composition  $\text{SiO}_2$ . The **silica** minerals include quartz, tridymite, cristobalite, coesite, stishovite, and several others. All silica minerals are tectosilicates having structures consisting entirely of  $\text{SiO}_4$  tetrahedra that share all of their oxygen atoms with adjacent tetrahedra. These minerals are **not** merely varieties of quartz having a different color (*e.g.* amethyst, rose quartz) or crystal size (*e.g.* jasper, agate, etc.). The silica minerals are different minerals with different structures, different symmetry, different physical properties, etc., but all with the same composition ( $\text{SiO}_2$ ). Two minerals that have the same chemical composition, but a different **crystal structure** are called **polymorphs**.
- Quartz** is the most common of the silica polymorphs. Actually, there are two polymorphs that have the name quartz:  $\alpha$ -**quartz** (low quartz) and  $\beta$ -**quartz** (high quartz). Both  $\alpha$ -quartz and  $\beta$ -quartz have structures based on helical arrangements of  $\text{SiO}_4$  tetrahedra with the “ridgepole” of one tetrahedron connected to the “keel” of the next tetrahedron in the spiral (see attached drawing).  $\beta$ -quartz is hexagonal with both 6-fold and 3-fold screw rotation axes. The  $\alpha$ -quartz structure is a distorted version of the  $\beta$ -quartz structure such that all of the screw-rotation axes are 3-fold. All of the quartz that you have ever held in your hand is  $\alpha$ -quartz. Because all screw rotation axes have a “hand,”  $\alpha$ - and  $\beta$ -quartz occur in both right- and left-handed forms. The chirality or “handedness” of a crystal of quartz can be determined by observing the direction of rotation of plane polarized light that passes through the crystal or by examining the crystal form in good crystals. It appears that right- and left-handed forms occur in equal numbers. Because quartz has no center of symmetry (crystal class 32), it has the physical property of **piezoelectricity**: it will develop an electrical potential when deformed or, conversely, it will deform when subjected to an electric field. The very strong piezoelectric effect in quartz is the basis for quartz oscillators, quartz watches, etc.
- Tridymite** and **cristobalite** are silica polymorphs that are found principally in siliceous volcanic rocks. For example, the “snowflakes” in snowflake obsidian are bundles of cristobalite crystals.  $\beta$ -tridymite and  $\beta$ -cristobalite both have structures based on layers of  $\text{SiO}_4$  tetrahedra with the individual tetrahedra alternately pointing up and down. These layers are stacked so that the upward pointing tetrahedra from one layer share oxygen atoms with the downward pointing tetrahedra in the layer above.  $\beta$ -tridymite is hexagonal and has these layers stacked in a hexago-



**tridymite layer**



**two cristobalite layers**

nal closest packing arrangement with a mirror plane between the layers and a repeat every other layer.  $\beta$ -cristobalite is cubic and has its layers stacked in a cubic closest packing arrangement with an offset between the layers and a repeat every third layer.  $\alpha$ -tridymite (orthorhombic) and  $\alpha$ -cristobalite (tetragonal) have structures that are distorted versions of the  $\beta$ -forms that occur at lower temperatures and have lower symmetry.

- The  $\alpha$ - and  $\beta$ -forms of quartz (and tridymite and cristobalite) are special polymorph pairs, because their structures have all the same bonds (they're topologically identical) but the atoms are in shifted positions (they're geometrically distinct). They are low and high temperature polymorphs of one another. At 1 bar pressure, the change from  $\alpha$ -quartz to  $\beta$ -quartz occurs very rapidly and **reversibly** at 573°C. Indeed, it is not possible to “quench”  $\beta$ -quartz;  $\beta$ -quartz exists **only** at temperatures above 573°C. Because the change from  $\alpha$ - to  $\beta$ -quartz occurs without the breaking of any bonds, this change is called a **displacive transformation**.
- The laws of thermodynamics predict that **only one** silica polymorph should be stable (occur at equilibrium) at any random temperature and pressure. Two silica polymorphs may be in equilibrium at special values of temperature and pressure. Three silica polymorphs may occur together at equilibrium at a single, unique temperature and pressure. In this sense, the silica polymorphs are like the different phases of H<sub>2</sub>O: ice, water, and steam. Given favorable kinetics, changing the physical conditions should lead to the change of one silica polymorph into another. For example, the  $\beta$ -quartz should change to  $\beta$ -tridymite at temperatures above 867°C (at 1 bar pressure). This change involves the breaking of bonds and, therefore, is called a **reconstructive transformation**. The experimentally determined temperature-pressure stability fields of the silica polymorphs are shown on the attached pressure-temperature diagram. Also shown are diagrams with the stability fields for the phases of H<sub>2</sub>O and for the polymorphs of ice. Note that the occurrence of any particular silica polymorph has the potential to provide information about the physical conditions in the rock at the time this mineral crystallized. For example, the mineral **stishovite** is believed to be formed on earth only due to the high pressures generated by a meteorite impact. The discovery of stishovite in a K/T boundary clay has been used as convincing evidence of a meteorite impact at the time of the K/T boundary.