



Typical hydrothermally grown synthetic crystals (left to right) blue-tinted quartz doped with cobalt; two yellow crystals of citrine, which is an iron-doped quartz; and colorless pure quartz

chemistry of hydrothermal solutions are largely due to the research of a small group of chemists and earth scientists, especially E. Ulrich Franck of the University of Karlsruhe, West Germany. Phase equilibria aspects of hydrothermal chemistry have been particularly emphasized by Rustum Roy and his students at Pennsylvania State University, where many critical oxide-water diagrams have been determined. Rare-earth oxide systems are currently being studied by Stanley Mroczkowski and others at Yale University.

The viscosity of water at temperatures above the critical temperature (374 °C) is between 3×10^{-4} and 14×10^{-4} poise, depending on density (or pressure), compared with a viscosity at room temperature of about 1×10^{-2} poise and at 100 °C and 1 bar of about 3×10^{-3} poise. This lower viscosity profoundly affects solvent behavior. Diffusion processes are more rapid, for example, so that solvent extraction of solids and crystal growth from solution are faster. Crystals grow slowly from solutions when diffusion is slow.

When diffusion is slow, too, concentration of the solute (and hence supersaturation) decreases near the interface between the crystal and the solution. As a result, minor fluctuations in concentration can lead the crystal to form protuberances into the growth solution.

Supersaturation is greatest at the tips of these protuberances, so that growth is fastest and farthest into the solution there. This phenomenon is called constitutional supersaturation. Growing crystals from a melt in the presence of impurities can result in the same phenomenon, which in this case is called constitutional supercooling.

The resulting protuberances can produce dendritic growth, in which columnar regions form on the grown crystal that often are misoriented to one another and frequently contain entrapped impurities. In the case of growth from solution, solvent often is entrapped. This mechanism accounts for the entrapment of liquid inclusions in minerals formed hydrothermally.

The object of synthetic crystal growth, of course, is to prepare as nearly a chemically and physically perfect bulk single crystal or single crystal film as is possible. Often a controlled concentration of some impurity (a dopant) is added to provide desired electrical and physical properties.

Crystals can be grown either from a system in which the only component present is the component forming the crystal (monocomponent growth) or from a system to which other components have been added (polycomponent growth). Growth also can take place from solids, liquids, or gases. Equilibrium can be shifted in the gas phase, liquid phase, or solid phase so as to favor the formation of the desired crystal.

Examples of the monocomponent growth of crystals from a solid include such solid-solid transformations as polymorphic transitions, the formation of crystals from a glass, and the annealing of a metal to remove strains. Solid-state precipitation is an example of polycomponent growth of crystals from a solid. Crystals are not usually grown from solids, however. Such growth is difficult to control because the solid matrix provides copious sites for crystal nucleation, making it difficult to transform a solid to a single crystal.

Monocomponent growth of crystals from a liquid—melt growth—takes place when the liquid is cooled to freezing. Melt growth is rapid, being limited, as a first approximation, only by the rate at which the heat of fusion can be dissipated. But high temperatures are required if the melting point of the material is high.

In growth from solution—polycomponent liquid growth—the additional component, the solvent, is used to “lower” the melting point of the material to be crystallized. A penalty must be paid for the privilege of crystallizing at a lower temperature, however. The solute must be diffused through the solvent to the growing crystal interface, and the solvent must be diffused away. Growth is slower, typically by a factor of 10 to 100.