CHAPTER III

THEORY

This chapter is explanation about the theories that accompany with this work. The theories about aluminas are shown in section 3.1. The theories about the crystal preparation are shown in section 3.2

3.1 Alumina

Aluminas are finding applications in many areas of catalysis.

Structures of aluminas

The term aluminas refer to three classes of compounds

1. Aluminum trihydroxides with the formula $Al(OH)_3$,
2. Aluminum oxyhydroxides with the formula $AlO(OH)$,
3. Aluminum oxides, in which it had transition phase and alpha alumina

(1). Aluminum trihydroxides

Three crystallized forms that meet the formula $Al(OH)_3$ may be distinguished: Gibbsite, Bayerite, Nordstrandite. The structure of these products can described by visualizing that two layers, A and B, of oxygen yield a Quasi-compact hexagonal packing. Aluminum ions occupy two-third of octahedral site generated by hexagonal packing. The three structures can be described by the packing order of layer A and B, as shown in Table 3.1 following. Figure 3.1 shows a model of Gibbsite structure.

Table 3.1: Packing order of different hydroxide

Gibbsite	Bayerite	Nordstrandite
B	B	A
A	A	B
A	B	B
B	A	A
B	B	B
A	A	A

(2). Aluminum oxyhydroxide

Three crystallized forms that meet the formula $AlO(OH).xH_2O$ may be distinguished: boehmite, an isotype of iron lepidocrocite and diaspore. It's useful to distinguish a third form, called pseudoboehmite, which is structurally derived, from boehmite but with specific properties.

Van Oosterhout (1960) described the structure of the corresponding iron compounds, which we use in aluminum compounds. In the direction of the a-axis there are HO-Al-O chains which are shown shematically in Figure 3.2. Two of these chains can be placed in positions antiparallel to each other in such a way of the first chain. The chains give both modifications a repetition distance of 2.85 A^o in the direction of a-axis. The difference between the two modifications is due to a different arrangement of the double molecules. The representation of the boehmite structure is shown Figure 3.3.

layers of the boehmite. Baker and Pearson (1974) proposed that this was due to extra water bond to Al atoms on the border of the sheets.

Since neither of these interpretations is consistent with the experimental result, Grebille (1983) has recently reanalyzed this problem. A model of stacking defects with a certain probability of existence is proposed. An excellent agreement may be observed between the calculated and measured values for defect amplitude of about 1 A°. This distance between blocks of normally spaced sheets is big enough to allow intercalation of water- 2 moles of AlO (OH) - and the excess water content can be well correlated to the shift of the (020) peak (through the probability of existence of this defect). Nevertheless, even if we think this is the best crystallographic model for pseudoboehmite, we are aware that some specific properties of these products are related to more sophisticated parameters, such as the presence of anions and alcoholates.
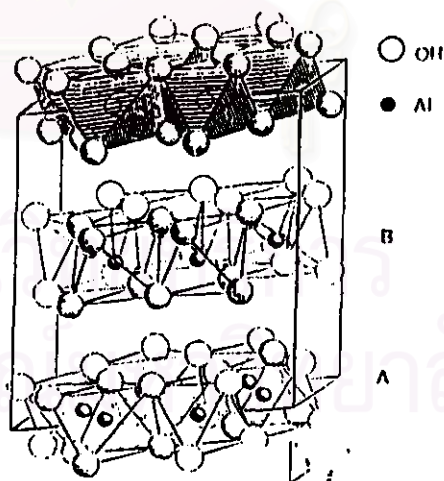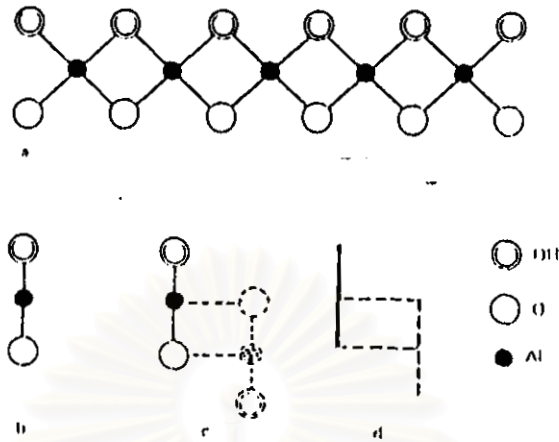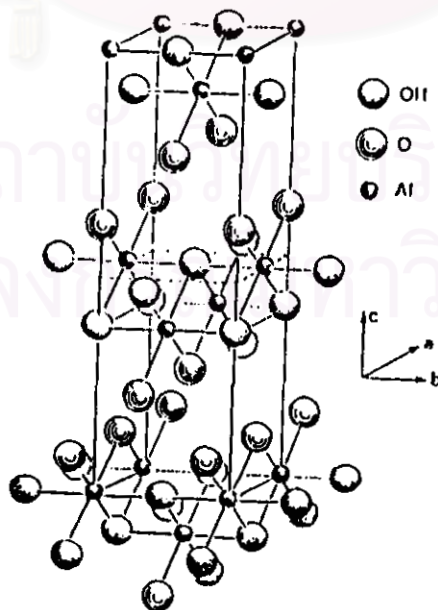

Figure 3.1 : Structure of gibbsite Al(OH)$_3$

Figure 3.2 : Schematic representation of boehmite ; (a) Al-O-OH chain ;(b) Profile of one chain ; (c) Profile of two antiparallel chains ; (d) Schematic representation of c

Figure 3.3 : Structure of boehmite AlO(OH)

Transition Aluminas

The partial dehydration of aluminum hydroxides and oxyhydroxides leads to compounds with the crude formula $Al2O3 \times H2O$ with $0<x<1$, which generally are poorly crystallized. These compounds are those used in such applications as catalyst supports, Claus catalysts, and adsorbents, which explains the interest shown in them. There are six principal phases designated by the Greek letters chi, kappa, eta, theta, delta, and gamma. The nature of the product obtained by calcination depends on the starting hydroxide (Gibbstie, boehmite and others) and on the calcination conditions. In effect, there exist several sequences during dehydration (Figure 3.4 and Table 3.2). In all cases, the ultimate product of dehydration is corundum ($Al2O3$).

An excellent bibliographical review of transition alumina has been complied by Leonard (1967). The situation can be reduced to a simple one on the basis of crystallographics, once one becomes aware that there are only two types of structures: spinel, for eta, gamma, delta, and theta and hexagonal, for chi and kappa. In chapter 4, we shall see that the differences find their origin mostly in the presence of defects or in the nature of the planes contributing to the surface area and that both are related to the nature of the starting hydroxide and the pseudomorphosis laws governing the structural change from the hydroxide to the oxide.
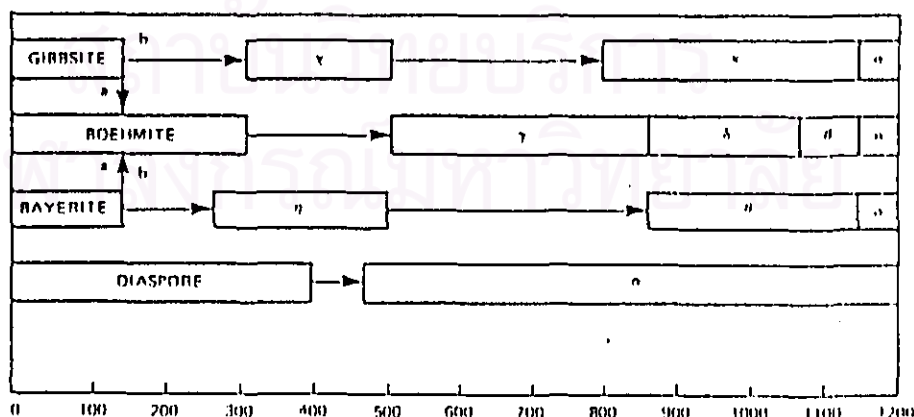

Figure 3.4 : Decomposition sequence of aluminum hydroxides

**Table 3.2** : Decomposition sequence of aluminum hydroxides

Conditions	Conditions favoring transformations	
	Path a	Path b
pressure	> 1atm	1 atm
atmosphere	mosit air	dry air
heating rate	> 1k / min	1k / min
particle size	>100 um	100 um

3.2 Growth of single crystals

Crystal may be grown from vapour, liquid or solid phases although, usually, only the first two give crystals of sufficient size to be in applications or for property measurements. A brief summary only is given of some of the various methods.

(1). Czochralski method

This is basically a method for the growth of a single crystal from a melt of the same composition. A seed crystal is placed in contact with (on the surface of) the melt, whose temperature is maintained slightly above its melting point. As the seed is gradually pulled out of the melt (Figure 3.5), the melt solidifies on the surface of the seed to give a rod-shaped crystal in the same crystallographic orientation as the original seed. The melt and growing crystal are usually rotated counterclockwise during pulling in order to maintain a constant temperature, melt uniformity, etc. The method is widely used for the growth of crystals of semiconducting materials, Si, Ge, Ga, As, etc.; usually an inert gas atmosphere at high pressure is used in order to prevent loss of As, P, etc. It has also been used to produce laser generator materials such as Ca $(NbO_3)_2$ doped with neodymium.
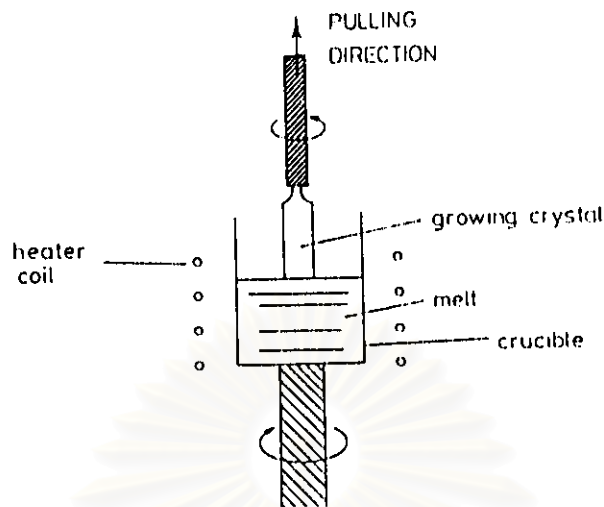
Figure 3.5 Czochralski method for crystal growth

2. Bridgman and Stockbarger methods

These methods are based on the solidification of a stoichiometric melt but, in these, oriented solidification of the melt is achieved by effectively passing the melt through a temperature gradient such that crystallization occurs at the cooler end. This is achieved in the Stockbarger method by arranging for a relative displacement of the melt and a temperature gradient (Fig 3.6a). In the Bridgman method, the melt is inside a temperature gradient furnace and the furnace is gradually cooled so that solidification begins at the cooler end (Fig 3.6b). In both methods it is again advantageous to use a seed crystal and atmospheric control may be necessary.

3. Zone melting

This is related to the Stockbarger method but the thermal profile through the furnace is such that only a small part of the charge is melted at any one time (Fig 3.6c). Initially that part of the charge in contact with the seed crystal is melted. As the boat is pulled through the furnace, oriented solidification onto the seed occurs and, at

the same time, more of the charge melts. This also forms a well-known method for the purification of solids, the zone-refining technique. It makes use of the principle that impurities usually concentrate in the liquid rather than in the solid phase. Impurities are therefore 'swept out' of the crystal by the moving molten zone. The method has been used for the purification and crystal growth of high melting metals such as tungsten.

## 4. Precipitation from solution or melt: flux method

In contrast to the above methods in which melts solidify to give crystals that have the same composition as the melt, precipitation methods involve the growth of crystals from a solvent of different composition to the crystals. The solvent may be one of the constituents of the desired crystal, e.g. crystallization of salt hydrate crystals using water as the solvent, or the solvent may be an entirely separate liquid element or compound in which the crystals of interest are partially soluble, e.g. SiO_2 and various high melting silicates may be precipitated from low melting borate or halide melts. In these cases, The solvent melts are sometimes referred to as fluxes since they effectively reduce the melting point of the crystals by a considerable amount. The method has recently used to grow crystals of β and β ''- alumina solid electrolytes using a borate flux. The importance of having information on the relevant phase diagram is stressed.

5. Epitaxial growth of thin layers

Single crystals in the form of thin layers are often required for application in electronic devices and special methods may be needed for their preparation. The use of a seed crystal in Czochralski and other methods implies an orientation relationship between the growing crystal and the seed. The crystal may grow epitaxially (two-dimensional structural relationship between seed and crystal) or topotaxially (three-dimensional relationship) on The seed. In The epitaxial growth of thin layers, oriented growth of the crystal occurs on the surface of a substrate. The substrate may be a crystal of the same or similar composition or it may be an entirely different material

whose lattice parameters, at its surface, match those of the growing crystal, to within a few percent. In This way, thin layers of GaAs have been grown from the vapor phase by deposition onto various substrates that include Al_2O_3, spinel $MgAl_2O_4$, Ge and ThO_2. Thin film crystals may also be prepares by epitaxial growth from liquids, in which case knowledge of the relevant phase diagram is necessary. In these methods, attention to the surface condition of the substrate is extremely important in order to ensure that it is as free from defects and impurities as possible.
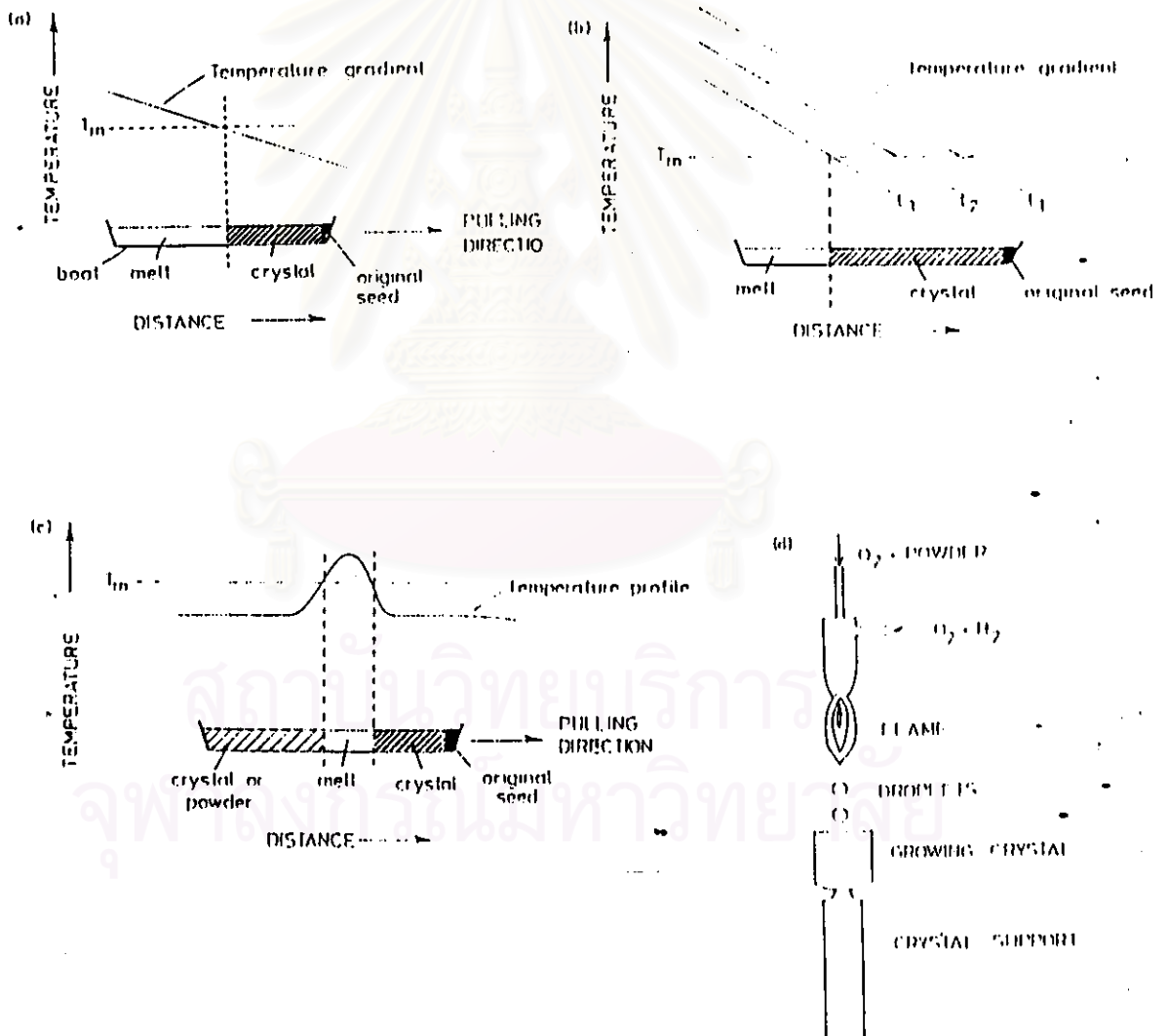
Figure 3.6 (a) Stockbarger method: T_m = crystal melting point. (b) Bridgman method: times t_1, t_2 and t_3 are shown. (c) Zone melting method. (d) verneuil method

6. Verneuil flame fusion method

This method was first used in 1904 for growing crystals of high melting oxides, including artificial gemstones such as ruby and sapphire. The starting material, in the form of a fine powder, is passed through an oxyhydrogen flame or some other high temperature torch or furnace (Figure 3.6d). After melting has taken place in The flame, The droplets fall on to the surface of the growing crystal or seed where they solidify, leading to crystal growth. The method has recently been used to prepare single crystals of CaO with a melting point ≈ 2600 °C by using a plasma torch to melt the CaO powder.

7. Comparison of different methods

For each crystalline substance, There are optimum conditions for satisfactory crystal growth. In preparing to grow crystals of a new material, much preliminary work, perhaps lasting several months, it needed in order to find suitable growth conditions. The quality of the resulting crystals therefore depends very much on the experimenters' skill. In addition, the various techniques that are available have certain intrinsic advantages and disadvantages; these are summarized in Table 3.3.

Table 3.3 : Comparison of crystal growth methods

Method	Advantages	Disadvantages
Melt growth (Czochralski, Bridgman-Stockbarger, Verneuil)	Rapid growth rates, giving large crystals; simple apparatus	Crystal quality may be poor with in homogeneities and large defect concentration
Solution growth (water crystallization, flux growth, hydrothermal method)	Isothermal conditions with slow growth rates give quality crystals of low defect concentration	Slow growth rates; problems of contaminant by container or flux

8. High pressure and hydrothermal methods

High pressure and hydrothermal methods are finding increasing applications in materials science and solid state chemistry. They are technologically important, both as an important method of crystal growth and for the synthesis of new materials with useful properties. They are also interesting scientifically since the use of high pressure provides an additional parameter or lever for obtaining fundamental information on the structures, behavior and properties of solids.

In most high-pressure methods, The sample is effectively squeezed between the jaws of opposed rams or anvils. Hydrothermal methods differ in that water under pressure is present inside the reaction vessel. For convenience, hydrothermal methods and their applications are outlined first, followed by other (dry) high pressure methods.

8.1. Hydrothermal methods

Hydrothermal methods utilize water under pressure and at temperatures above its normal boiling point as a means of speeding up the reactions between solids. The water performs two roles. The water-as liquid or vapour-serves as the pressure transmitting medium. In addition, some or all of the reactants are partially soluble in the water under pressure and these enable reactions to take place in, or with the aid of, liquid/or vapour phases. Under these conditions,reactions may occur that, in the absence of water, would occur only at much higher temperatures. the method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Since hydrothermal reactions must be carried out in closed vessels, The pressure-temperature relations of water at constant volume are important. These are shown in Figure 3.7. The critical temperature of water is 374 °C. Below 374 °C , two fluid phases,liquid and vapour , can coexist. Above 374 °C only one fluid phase, supercritical water, ever exists. Curve AB represents the saturated steam curve. At pressures below this curve liquid water is absent and the vapour phase is not saturated with respect to steam; on the curve the vapour is composed of saturated steam which is in equilibrium with liquid water; above the curve, liquid water is effectively under compression and the vapour phase is absent.

The dashed curves in Figure 3.7 may be used to calculate the pressure that is developed inside a vessel after it has been partially filled with water, closed and heated to a certain temperature. Thus, curve BC corresponds to a vessel that is initially 30 percent full of water: at, for example, 600 °C, a pressure of 800 bar is generated inside the closed vessel. Although Figure 3.7 applies strictly to pure water, the curves are modified little, provided the solubility of solids present in the reaction vessel is small.

The design of hydrothermal equipment is basically a tube, usually of steel, closed at one end. The other end has a screw cap with a gasket of soft copper to provide a seal. Alternatively, 'the 'bomb' may be connected directly to an independent pressure source, such as a hydraulic ram; this is known as the ' cold seal' method. The reaction mixture and an appropriate amount of water are placed inside the bomb, which is then sealed and placed inside an oven at the required temperature.
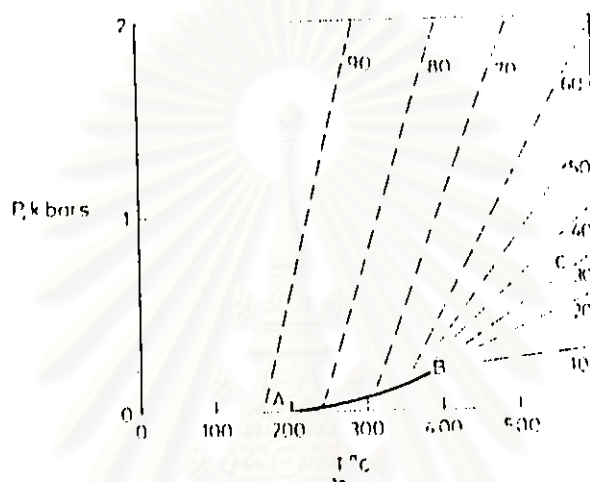
Figure 3.7 Pressure-temperature relations for water at constant volume. Dashed curves represent present pressures developed inside a closed vessel; numbers represent the percentage degree of filling of the vessel by water at ordinary P,T. (After Kennedy, 1950)

(a) Synthesis of new phases

Calcium silicate hydrates. Hydrothermal methods have been used successfully for the synthesis of many materials. A good example is the family of calcium silicate hydrates, many of which are important components of set cement and concrete. Typically, lime, CaO and quartz, SiO_2, are heated with water at temperature in the 150 to 500 °C and pressures of 0.1 to 2.0 kbar. Each calcium silicate hydrate has, for its synthesis, optimum preferred conditions of composition of starting mix, temperature, pressure and time. For example, xonotlite, $Ca_6Si_6O_{17}(OH)_2$, may be preheated by heating equimolar mixtures of CaO and SiO_2 at saturated steam pressures in the range 150 to 350 °C. by varying the experimental conditions, H.F.W. Taylor and others have been able to unravel the chemistry of this complex family of solids.

(b) Growth of single crystals

For the growth of single crystals by hydrothermal methods it is often necessary to add a mineralizer . A mineralizer is any compound added to the aqueous solution that speeds up its crystallization. it usually operates by increasing the solubility of the solute through the formation of soluble species that would not usually be in the water. For instance, the solubility of quartz in water at 400 °C and 2 kbar is too small to permit the recrystallization of quartz, in a temperature gradient, within a reasonable space of time. On addition of NaOH as a mineralizer, however, large quartz crystals may be readily grown. Using the following condition, crystals of kilogram size have been grown: quartz and 1.0 M NaOH solution are held at 400 °C and 1.7 kbar; at this temperature some of the quartz dissolves. A temperature gradient is arranged to exist in the reaction vessel and at 360°C the solution is supersaturated with respect to quartz which precipitates onto a seed crystal. In summary, therefore quartz dissolves in the hottest part of the reaction vessel, is transported throughout the vessel via convection currents and is precipitated in cooler parts of the vessel where its solubility in water is lower. Quartz single crystals are used in many devices in radar and sonar, as piezoelectric transducers, as monochromators in X-ray diffraction, etc. Annual world production of quartz single crystal, using hydrothermal and other methods, is currently a staggering 600 tons!

Using similar methods, many substances have been prepared as high quality single crystals, e.g. corundum (Al_2O_3) and ruby (Al_2O_3 doped with Cr^{3+}).

8.2. Dry high-pressure methods

Techniques are now available for generating static pressures of several hundred kilobars at both ambient and high temperatures; using shock wave methods the attainable P,T range may be extended still further. Experimental techniques are not detailed here since the techniques are rather specialized. They vary from a simple 'oppose anvil' arrangement, whereby the sample is effectively squeezed between two

pistons or rams, one of which is fixed and the other connected to a hydraulic jack, to more complex designs in involving three or four anvils or rams.

Applications: Synthesis of unusual crystal structures. Phases synthesized at high pressures tend to have higher densities than phases synthesized at atmospheric pressure and this sometimes gives rise to unusually high coordination numbers (see also Chapter 12). For example, the coordination of silicon in SiO_2 and the silicates is, with very few exceptions, tetrahedral. An exception is one of the high-pressure polymorphs of siO_2, called stishovite, which is formed at pressures above 100 to 120 kbar. Stishovite has the rutile structure and therefore contains octrahedrally-coordinated silicon. Some other examples of increases coordination number in high pressure polymorphs in Table 3.4
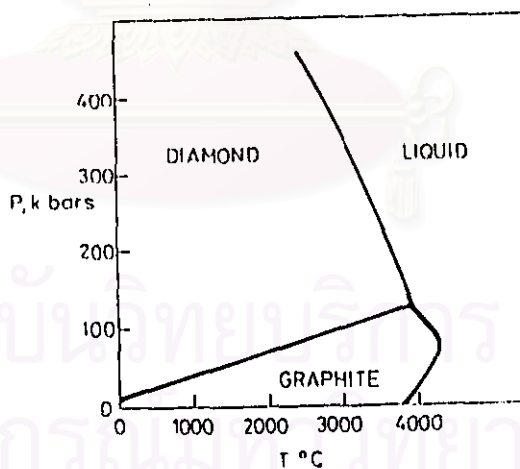
Figure 3.8 The P, T phase diagram for carbon. (After Bundy, 1963)

Table 3.4 : High pressure polymorphism of some simple solids

Solid	Normal structure and coordinatation number	Typical transformation conditions		High pressure structure and coordination number
		P(kbar)	T(°C)	
C	Graphite,3	130	300	Diamond, 4
CdS	Wurtzite 4:4	30	20	Rock salt 6:6
KCl	Rock salt 6:6	20	20	CsCl, 8:8
SiO_2	Quartz 4:2	120	1200	Rutile, 6:3
Li_2MoO_4	Phenacite 4:4:3	10	400	Spinel, 6:4:4
$NaAlO_2$	Ordered Wurtzite 4:4:4	40	400	Rock salt 6:6:6

By use of high pressures at is possible to stabilize ions in unusual oxidation sates, such as Cr^{4+}, Cr^{5+} Cu^{3+}, Ni^{3+} and Fe $^{4+.}$ Thus chromium normally occurs as Cr^{3+} and Cr^{6+} with octahedral and tetrahedral coordination, respectively. However, various peroskite phases containing octahedrally coordinated Cr^{4+} have been prepared at high pressures, such as $PbCrO_3$, $CaCrO_3$, $SrCrO_3$, and $BaCrO_3$.

Possibly the main industrial application of high-pressure methods is in the synthesis of diamonds from graphite. Suitable thermodynamic conditions for the transformation are given by reference to the P, T phase diagram for carbon, given in Figure 3.8, although the transformation rates are slow, even at pressures and temperatures that are well within the diamond phase field.