Synthesis in strong fluoride solutions KF, RbF, and CsF increases the growth rate, however, further increase in the concentration of F leads to the formation of fluoroniobates and fluorotantalates of alkali metals: Me_2NbF_7 and Me_2TaF_7. Obviously, such concentrated solutions do not give 100% niobates and tantalates of Bi and Sb. It has been found that in aqueous solution of KHF_2, even the formation of complex niobate K_2SbNb_2O_15 takes place.

Thus, the hydrothermal method is a most valuable tool for the synthesis of a variety of simple and complex niobates and tantalates. However, a complete understanding of the growth technology for these compounds insists on systematic investigations of various aspects of the growth parameters, like temperature, pressure, pH, type of nutrient, and solvent.

8.13 HYDROTHERMAL SYNTHESIS OF ARSENATES

Arsenates are closer to phosphates and vanadates in their mineralogy and crystal chemistry. There are several arsenate minerals occurring in nature, like mimetite, (PbCl) Pb_4 (AsO_4)_3, tilasite (MgF) CaAsO_4; adelite [(MgOH)CaAsO_4], sarkinite [(MnOH) MnAsO_4], olivenite [Cu_2(OH) AsO_4], adamite [Zn_2(OH)AsO_4], clinoclasite (6CuO·As_2O_3·3H_2O), soselite (Ca,Co,Mg)_3, As_2O_8·2H_2O, and so on. However, the number of arsenate minerals is much less than the number of vanadates and phosphates. The same is the case with reference to the synthetic analogs, i.e., the number of synthetic arsenates is much less than the number of synthetic phosphates and vanadates. Hence, in comparison with the rich structural chemistry of transition metal phosphates, reports on the arsenates are rare. Although a few arsenates have stoichiometries similar to those of the phosphate analogs, their structures are considerably different. Most of these arsenates adopt new structural types and have stoichiometries not found in the phosphates. The hydrothermal technique helps immensely to obtain new structures among arsenates. Some of the arsenates synthesized belong to the NASICON family (Na,Zr_2(AsO_4)_3; A^{2+}B^{2+}As_2O_5 (A = Ca, Sr, Ba; B = Cu), both exhibiting superionic properties, NaNb_2AsO_8 with nonlinear optical properties, ABXO_4 type [A = Mn, Zn, Cu^{2+}, Co^{2+}, Mg^{2+}, etc.; B = (OH); X = As], several complex arsenates showing unique structures related to geolites. In spite of a wide structural diversity, the hydrothermal synthesis of arsenates is not very
popular owing to the best known reasons, that arsenic is highly corrosive and highly reaction susceptible. Also, it contaminates the system unless the experiments are carried out at $T < 300^\circ C$ using teflon liners.[132]-[136]

The majority of experiments in recent years have been carried out in stainless steel autoclaves provided with teflon lining. However, the high temperature experiments, like in the case of NaNb$_2$AsO$_8$, are carried out in sealed gold liners, at $T = 750^\circ C$ and $P = 32,000$ psi.

For example, the copper diarsenates (ACuAs$_2$O$_7$, A = Ca, Sr, Ba) synthesis has been carried out in teflon-lined autoclaves at $230^\circ C$ for four days, followed by a slow cooling to room temperature at $50^\circ C$/hr. The pure phase is obtained by heating a mixture of Me$^{2+}$ (OH)$_2$ (Me$^{2+}$ = Ca, Sr, Ba), CuO, KCl, H$_3$AsO$_4$, pyridine and water, in the following molar ratios:

- Ca$^{2+}: Cu : As = 1:2:7.5$
- Sr$^{2+}: Cu : As = 1:4:15$
- Ba$^{2+}: Cu : As = 1:2:7.5$

The crystal chemical study of these $A^2B^{2+}As_3O_7$ compounds shows that the As$_3$O$_7$ group is very adaptive to the bonding requirements of other groups in the structure by adjusting the As-O-As bond angle and the torsional angle between the two AsO$_4$ tetrahedra. The size of the alkali-earth metal cation seems not to play an important role in deciding the structural types of the arsenates as it does on the corresponding phosphates.

The complex arsenates, like (Mg$_x$Ni$_{1-x}$)(OH)(AsO$_4$)$_2$, could be prepared using hydrothermal conditions and starting from the (Mg$_{3-x}$Ni$_x$)(AsO$_4$)$_2$.8H$_2$O (X = O, O.5) precursors. The starting compounds were at $180^\circ C$ in a teflon-lined steel autoclave 90% filled.[132]

Chou and Kanatzidis (1996) have synthesized the novel type of transition and main group metal polychalcogenides, and some of them are inaccessible by traditional solution methods.[137] These authors have used organic counter-ions $R_4E^+$ (E = P, R = Ph; E = N, R = alkyl) to synthesize these polychalcoarsenates.

With the recent discovery of several nonlinear optical properties among arsenates, like in KTiOAsO$_4$, there is a growing interest for new NLO materials from the arsenate family.[138] Among these, NaNb$_2$AsO$_8$ is an important material showing a great promise as second harmonic generator material.[136]
Thus, the growth of complex coordinated compounds like sulphides, selenides, tellurides, and arsenates under hydrothermal conditions, is very important.

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9

Hydrothermal Synthesis of Native Elements and Simple Oxides

9.1 INTRODUCTION

The hydrothermal technique is very useful for growing crystals of native elements and simple oxides. The native element crystals popularly grown under hydrothermal conditions are gold, silver, platinum, copper, arsenic, cobalt, nickel, tellurium and bismuth related compounds. Similarly, among the hydrothermally produced oxides, zincite, rutile, zirconia, and hafnia are very popular. In fact, the hydrothermal method is the only suitable method for the growth of these compounds for various reasons like high melting point, very low solubility, acid resistance and so on. In this chapter, we describe the hydrothermal synthesis of selected native element crystals.

9.2 HYDROTHERMAL SYNTHESIS OF NATIVE ELEMENTS

The hydrothermal technique is especially suitable for obtaining pure and high quality crystals of elements. The interest in the synthesis of these elements has rejuvenated, particularly after the discovery of noble metals in seafloor hydrothermal mineralization.\[1\][2] Gold, silver, iridium, palladium, platinum, etc. have been reported in hydrothermal mineralization from two mid-oceanic ridges: Juan de Fuca and Mid-Atlantic at
The solubilities of noble metals in hydrothermal fluids are highly relevant to the redistribution and possible concentration of these metals by the action of water-rich fluids on magmatic occurrences.

The hydrothermal synthesis of noble metals takes place through two types of reactions:

\[
\text{Eq. (1)} \quad 2\text{Me (s) + 2 (OH)\text{- (l)}} \rightarrow 2\text{MeOx (l) + H}_2\uparrow \\
\text{Eq. (2)} \quad 2\text{Me (s) + 2 (Hl) (l)} \rightarrow 2\text{MeL (l) + H}_2\uparrow 
\]

where L = acid anion (ligand).

The first reaction is characteristic of alkali solutions and the second reaction is characteristic of acids. In both the cases, hydrogen helps in establishing equilibrium. As a result of this, the desired metal crystallizes. If temperature gradient is maintained in the autoclave, the reaction route is determined by the Eh of metals from temperatures. Therefore, in one case, the crystallization of native metal crystals takes place in the hotter zone, and in the other case, in the cooler zone. Thus, the hydrothermal crystallization of metals is possible in both acid and alkali solutions. It is possible to obtain the entire series of metals as single crystals when an oxidizing agent like halogenide is used.\[^{[3]}\] The crystallization takes place in quartz ampoules with external control of the CO\textsubscript{2} gas at temperatures 440–600°C and temperature gradients 30–120°C in aqueous solutions of HCl, HI, HBr and the crystals obtained are: Au, Ag, Pt, Co, Ni, Te and As. In this regard, it is appropriate to emphasize the work of Rabenau and Rau (1968) on the hydrothermal synthesis of gold crystals.\[^{[4]}\] In aqueous solutions of HI at 500°C, the well-soluble [AuI\textsubscript{4}]\textsuperscript{-} complexes are formed, their stability depends upon the temperature, and it falls with destabilization of [AuI\textsubscript{4}] complexes and the formation of gold crystals:

\[
\text{Eq. (3)} \quad \text{Au + 4HI \rightarrow [AuI}_4]\textsuperscript{-} + 2\text{H}_2\uparrow 
\]

The first attempt of gold crystallization from aqueous solutions was demonstrated by Bujor (1948) under hydrothermal conditions at 390°C and 300 atm and cubic crystals of gold were obtained.\[^{[5]}\]

Honma et al. (1991) have studied, in detail, the dissolution and precipitation of gold and silver at 150°C in various strong acid solutions and aqueous NaHS over periods of 60 to 120 days.\[^{[6]}\] The alloy Au\textsubscript{90}Ag\textsubscript{50} was used as the starting material. For the first time millimeter-sized free-growing enhenadal crystals of pure gold were obtained from 6N HCl.
solution after 120 days, and no precipitation of either gold or silver was obtained from the sulfuric acid and nitric acid solutions. Small crystals of both electrum (Au$_{71}$Ag$_{29}$) and argentite were precipitated onto the starting alloy sample after 120 days in 5.2 M aqueous NaHS.$^{[6]}$

Gold solubility has been studied extensively by several authors in HCl aqueous solution and others.$^{[7]}$–$^{[12]}$ Seward and his group have done excellent work on the complexing and solubility of gold and other noble metals under hydrothermal conditions, especially in the aqueous sulphide solutions at temperatures between 150 and 500°C and pressure of 500–1500 bar over a wide range of pH.$^{[12]}$–$^{[14]}$ They have derived stability constants for the complexes AuHS and Au(HS)$_2$. It can be used to quantitatively model the transport of gold in natural hydrothermal fluids to understand the mechanisms and conditions of gold deposition. It has been shown that in sulphide solutions at near neutral pH, the complex Au(HS)$_2$ is the dominant gold species. The solubility of gold reaches a maximum where pH = pK of H$_2$S. However, with increasing temperatures, the pK$_1$ of H$_2$S shifts towards more alkaline values (Suleimenov and Seward, 1995) and, therefore, the maximum solubility due to this species also shifts to more alkaline pH.$^{[15]}$ In acid-pH, high-temperature solutions, the neutral species AuHS$^+$, therefore, will be the dominant gold transporting species and, although the gold solubility may be 1–2 orders of magnitude lower than the solubility at pH > pK$_1$ (H$_2$S), this complex has to be taken in to account when such systems are modeled. The main reason for the decreasing solubility of gold in high-temperature sulphide solutions is the change in pH and/or total reduced sulphur concentration. The effect of temperature on the solubility of gold in sulphide solutions is very strongly related to the total sulphur concentration and the hydrothermal fugacity.

Crystallization of copper, silver, selenium and tellurium in alkaline solutions takes place in aqueous solutions of hydroxides of alkali metals at partial pressure of hydrogen, 0.5–40 atm, water pressure > 600 atm, and temperature 350–550°C. For obtaining fairly large crystals, the experiments are carried out with temperature gradients, and in autoclaves with or without different liners. Glass carbon ampoules are most effective in this respect. In experiments at $T < 300$°C, Teflon$^\circledR$ liners are used. As nutrient, respective metal oxide powders or metal pieces are used.

Popolitov (1969), and Popolitov and Litvin (1970) have studied the systems Sb-Te-I(Br)-H$_2$O and obtained the crystals of Se and Te. They proposed a simple method of synthesis of Se and Te crystals in aqueous solutions of hydrochloric acid in autoclaves provided with quartz ampoules.$^{[16]}$$^{[17]}$
The octahedral or more complex form of single crystals of copper have been obtained in the cooler zone of the autoclave containing aqueous solutions of NaOH KOH. In highly concentrated aqueous solutions of hydroxides of alkali metals and at $P_{H_2O} > 50$ atm, often the plate-like crystals form with (110) faces exhibiting highly vitreous luster, and the crystal size varies from 1–3 mm.[18]

Silver crystallization conditions are very close to those of crystallization of copper. Crystals are usually plate-like and show twinning. The crystal surfaces exhibit metallic luster with a rise in temperature and silver dendrites form, resembling its appearance in nature. The size varies from 0.1 to 0.5 mm.[19]

Selenium crystals have been obtained under hydrothermal conditions by Kolb and Laudise (1971). The crystals are needle-like prismatic with metallic luster, color light-grey. The size of the individual needles or crystals is up to 10–12 mm with a thickness of 0.2–0.3 mm.[20]

Tellurium crystals have been obtained in aqueous NH₄Cl solutions (8–15 wt%) at temperatures 450–550°C, the partial pressure of hydrogen ~ 80 atm and $P_{H_2O}$ 600 atm with a rise in the concentration of the solvent (up to 20 wt%). The skeleton-like forms appear.[21]

Diamond synthesis has become a very important activity. Several research organizations and corporations have taken up diamond synthesis as a challenge in solid state science. Man started using diamond several centuries B.C. At that time, diamond was thought of as a hard glass. When cutting technology was discovered in the 17th century, man began to use diamond as an aristocratic jewel.

Industrial application of diamonds started in the beginning of the 20th century and the first application of diamond was in a grinding wheel. The wheel consisted of diamond powder with metal (or polymer) binder, which can be called a refined material.

In 1955, diamond was produced artificially and the success was closely related to the discovery of high-pressure technology. This technology was later applied to the production of sintered diamond, which can be categorized as a refined artificial material. This technology was also applied to the production of cubic boron nitride (CBN), which is a completely artificial material. The greatest discovery related to diamond was its synthesis from the gas phase for the first time by Deriaguin et al. in 1976, and Matsumoto et al. (1982).[22][23] Although many methods have been reported for diamond synthesis from the gas phase, all methods are
basically modified chemical vapor deposition methods. Diamond made by
t hese methods, therefore, is referred to as CVD diamond. About seventeen
years ago, no one could have conceived that diamond would become an
electronic material. People considered a diamond mainly as a jewel, but
the discovery of diamond synthesis from the gas phase changed that image
dramatically.

The authors believe that the unique properties of diamond contrib-
uted to the enhancement of research on the material, resulting in a wide
range of research with hope for new applications.

There are three major processes of diamond synthesis: i) high-
pressure–high-temperature (HPHT), and ii) chemical vapor deposition
(CVD), (which are at least 40 and 30 years old respectively), and iii) low-
pressure solid state source (LPSSS). Bundy et al. (1955) at General
Electric Co., announced their success in synthesizing diamond under
HPHT conditions. A few tons of industrial diamond abrasive grains are
made this way each year in various factories around the world. De Vries
(1987) reviewed CVD diamond synthesis in detail. Roy and his group
of researchers have worked out the growth technology for diamond using
LPSSS method in detail. Figure 9.1 shows the schematic diagram
comparing three popular methods of diamond synthesis.

It is interesting to note that the nucleation and growth kinetics had
won out over thermodynamics. The CVD process represents the field
outside the $P-T$ stability region for diamond. Figure 9.2 shows the phase
diagram for carbon crystalline phases. The equilibrium data for material
trapped in inclusions in diamonds indicates final temperatures of 600–
800°C and pressures up to 10 MPa. De Vries (1990) has argued a case for the possibility of growing
diamonds under hydrothermal conditions, and several researchers have
presented various attempts. Szymanski et al. (1995) have carried out
diamond synthesis using relatively low-pressure liquid phase epitaxy on
seeds, in an autoclave filled with a specially prepared water solution.
Natural diamonds of 0.22 gm and 0.49 were used as seeds. The solution
and seeds were subjected to 170 MPa and 400°C for 21 days. A thin
irregular (15–14 µm) colorless film of polycrystalline diamond on the
natural (111) faces of the seed crystals was obtained (Fig. 9.3). This work
shows that hydrothermal synthesis may be an effective way for homo- and
heteroepitaxy of diamond as a continuous layer on seed material surfaces
of diversified shape and possibly for growth of large diamonds on seeds.
Figure 9.1. Schematic diagram comparing three popular methods of diamond synthesis processes.\textsuperscript{[27]}
Recently, Yamaoka and Akaishi (1999) reported the growth of diamond under HPHT water conditions. The basic principle used by these authors is that carbon reacts with high-temperature water (vapor) producing so called “water gas.” It is natural to expect that graphite reacts with water and precipitates as diamond under high-pressure–high-temperature (HPHT) conditions in the thermodynamically stable region of diamond. The authors have used three types of capsules to carry out the diamond synthesis under HPHT conditions: i) Ta cylindrical containers,
ii) Mo double capsules, and iii) conventional point sealed capsules. The selection of these capsules depends upon the duration of the experiments and the pressure-temperature conditions. Figure 9.4 shows the diamond growth under HPHT conditions. This work shows that graphite reacts with HPHT water and precipitates as diamond in the regions of 1300–2200°C and 5.5–7.7 GPa. The reaction proceeded more rapidly with increasing pressure and temperature.

Figure 9.4. Diamond growth under HPHT conditions.[34]

Suito and Onodera (1999) have synthesized diamond using phenolic resins between 1.6 and 4 GPa and cobalt at 10 GPa with calcium carbonate as catalyst-solvents.[35] In this case, the pressure and temperature conditions of diamond synthesis depended upon the pre-firing temperatures. Well-defined single crystals of 0.3–0.7 mm in size were obtained at 4 GPa and 1500°C (Fig. 9.5).

However, the diamond synthesis in the presence of metal powder, molten high molar alkali solution, and water at 800°C and 1.4 kbar pressure range is the most popular technique. The growth rate is quite low. The crystals obtained are usually 5–10 microns in size. Several types of
starting materials have been tried for the synthesis of diamond. The most important aspects are the behavior of carbon under high-pressure–temperature conditions, the presence of a matching substrate, then preferential oxidation of \( sp \)-bonded C by water. Thermodynamically diamond is stable at temperatures < 800°C. Graphitization of the diamond surface should be prevented. The most important thing is to bring carbon into the high-energy state under hydrothermal conditions and arrest it.

Figure 9.5. Diamond single crystals.\textsuperscript{[35]}

On the whole, the growth of diamond crystals is a challenging task because of the lack of knowledge of the pH of the growth media, halogen problem, very slow growth rates, lack of solubility data, the solvent chemistry, and so on. Therefore, the current situation in diamond synthesis can be compared to that of quartz growth some one hundred years ago. The coming five years will decide the future of diamond research.

In the recent years, carbon nanotubes, particularly the multiwall nanotubes, are becoming materials of great potential in the next generation of electronic nanodevices. Recently, multiwall open-end and closed carbon nanotubes with wall thickness from several to more than 100 carbon layers have been produced by the hydrothermal method by Yoshimura and his team of researchers at Tokyo Institute of Technology, Japan, jointly with the University of Illinois, Chicago, USA, (by Yuri Gagosti) using water-based mixtures in the presence of a catalyst like nickel at 700–800°C under 60–100 MPa pressure. The most significant factor of this work is the use of very low cost materials like polyethylene and water as raw materials. A controlled growth of super-long carbon nanotubes may be possible in autoclaves with temperature gradient. The reader can find more information on carbon nanotubes in the proceedings of the Joint International Symposium on Hydrothermal Reactions and International Conference on Solvothermal Reactions (Joint ISHR & ICSTR) held in Kochi, Japan, during July 25–28, 2000.
9.3 HYDROTHERMAL SYNTHESIS OF HYDROXIDES

The hydrothermal method is popularly used in the synthesis of single crystals of hydroxides of several divalent and trivalent metals. Usually the field of stability is expanded by the presence of surplus water during the transition reaction oxide ⇔ hydroxide, and temperature of the system. In this regard, the alkali metal hydroxide solutions are more effective. Table 9.1 gives the list of the metal hydroxides obtained by hydrothermal methods, and their experimental conditions.[36] The experimental temperatures and pressures vary from 100 to 600°C and 6 atm to 4000 atm.

Table 9.1. Hydrothermal Experimental Conditions of Synthesis of Hydroxides[36]

<table>
<thead>
<tr>
<th>Hydroxide</th>
<th>Solvent</th>
<th>T°C</th>
<th>P, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(OH)₂</td>
<td>H₂O</td>
<td>100–175</td>
<td>4000</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>3% NaOH</td>
<td>450</td>
<td>600</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>3% NaOH</td>
<td>550</td>
<td>650</td>
</tr>
<tr>
<td>Cd(OH)₂</td>
<td>35% NaOH</td>
<td>450</td>
<td>1000</td>
</tr>
<tr>
<td>Mn(OH)₂</td>
<td>5% NaOH</td>
<td>450</td>
<td>1000</td>
</tr>
<tr>
<td>Co(OH)₂</td>
<td>1% NaOH</td>
<td>280</td>
<td>3500</td>
</tr>
<tr>
<td>Ni(OH)₂</td>
<td>1% NaOH</td>
<td>280</td>
<td>3500</td>
</tr>
<tr>
<td>TR(OH₃)</td>
<td>15% NaOH</td>
<td>350</td>
<td>600</td>
</tr>
<tr>
<td>TR = La-Gd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TR = Dy, Er, Yb</td>
<td>15% NaOH</td>
<td>450</td>
<td>600</td>
</tr>
<tr>
<td>Cr(OH)₃</td>
<td>3% NaOH</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>In(OH)₃</td>
<td>40% NaOH</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>H₂O</td>
<td>&lt; 150</td>
<td>39</td>
</tr>
<tr>
<td>In(OH)₃</td>
<td>H₂O</td>
<td>185–275</td>
<td>50–75</td>
</tr>
<tr>
<td>In(OH)₃</td>
<td>D₂O</td>
<td>180–210</td>
<td>18–50</td>
</tr>
<tr>
<td>InOOH</td>
<td>H₂O</td>
<td>325–410</td>
<td>120–800</td>
</tr>
<tr>
<td>InOOD</td>
<td>D₂O</td>
<td>360–380</td>
<td>320–400</td>
</tr>
<tr>
<td>α -ScOOH</td>
<td>H₂O</td>
<td>162–350</td>
<td>6–170</td>
</tr>
<tr>
<td>β -ScOOH</td>
<td>H₂O</td>
<td>350</td>
<td>160</td>
</tr>
<tr>
<td>Y(OH)₃</td>
<td>H₂O</td>
<td>300</td>
<td>85</td>
</tr>
<tr>
<td>CrOOH</td>
<td>H₂O</td>
<td>450</td>
<td>2700</td>
</tr>
<tr>
<td>GdOOD</td>
<td>D₂O</td>
<td>600</td>
<td>1400</td>
</tr>
<tr>
<td>SmOOH</td>
<td>H₂O</td>
<td>600</td>
<td>1400</td>
</tr>
<tr>
<td>Sr₂Cr₂(OH)₁₂</td>
<td>H₂O</td>
<td>150–200</td>
<td></td>
</tr>
</tbody>
</table>
Hydrothermal synthesis of Mn(OH)$_2$, Cd(OH)$_2$, Co(OH)$_2$ and Ni(OH)$_2$ crystals depend upon the partial pressure of hydrogen ($P_{H_{2}O} > 10$ atm). Some of the hydroxide crystals like Mg(OH)$_2$, Mn(OH)$_2$, Co(OH)$_2$ form fairly large size crystals of 5–10 × 5–10 mm size with a thickness of 0.1 mm. The other hydroxide crystals are small (0.1 mm). The double distilled water is usually used in the synthesis of hydroxides. The temperature gradient method gives single crystals of hydroxides. The oxyhydroxides (MeOOH) often crystallize at relatively higher temperatures. Among these, the polymorphism is very common, and it depends upon the temperature, for example in rare earth hydroxides.$[37]$

Similar to the alkali solutions in the synthesis of metal hydroxides, acid solutions, particularly chloride solutions, are also used. Thus, in this case, an increase in the concentration of the solution forms hydroxychlorides, often with 100% output. Their synthesis takes place as a result of the substitution of one hydroxyl group with chloride as follows:

\[ \text{Me} (\text{OH})_3 + \text{HCl} \rightarrow \text{Me} (\text{OH})_2\text{Cl} + \text{H}_2\text{O} \]

In this way Demianets and Emelyanova (1969) have obtained hydroxyl-chlorides of neodymium, Nd(OH)$_2$Cl, under hydrothermal conditions using aqueous solutions of NH$_4$Cl (concentration 7 wt%) at temperatures 450–480°C.$[38]$ At 500°C, rare earth hydroxyl-chlorides, R(OH)$_2$Cl, where R = La, Ce, Pr, Nd, Sm, Gd, have been obtained by Kletsov et al. (1973).$[39]$ Similarly, Carter and Levinson (1969) have obtained hydroxyl-chlorides containing La, Nd, Sm, Gd, Y, and the more complex hydroxyl-chloride of ytterbium, Yb$_2$O(OH)$_5$Cl$_2$, using acidic chloride solutions at 1400 atm pressure and 550°C.$[40]$ Under hydrothermal conditions, the chloride group can be replaced by carbonate ions with the formation of hydroxyl carbonate, R(OH)CO$_2$.$[41]$ Similarly, Christensen and Hazle (1969) have obtained mixed hydroxides of type MeSn(OH)$_6$, where Me = Ca, Mn, Fe, Co, Zn, through the interaction of aqueous solutions of NaSnO$_3$ with chlorides or nitrates of respective metals.$[42]$ Wolski et al. (1997) have obtained Mn$_x$Fe$_{2-2x}$ (OH)$_{6-4x}$ which find numerous applications in technology.$[43]$ For certain $x$ values, the initially amorphous mixtures, Mn$_x$Fe$_{2-2x}$ (OH)$_{6-4x}$, are converted into ferromagnetic species when stored as water suspensions well below 100°C, and the higher the temperature, the shorter the time of transformation. Aqueous solutions of titrated 0.25 M Fe (III) nitrates, mixed together in the desired proportions to give the hydroxide mixtures Mn$_x$Fe$_{2-2x}$ (OH)$_{6-4x}$ in 0.1x intervals,
were treated by constant stirring with 2M NaOH till pH 9.5 was reached, to ensure full Mn$^{2+}$ precipitation and at the same time to avoid oxidation to Mn$_3$O$_4$ and $\beta$-MgOOH at higher pH. The washed and filtered hydroxides were placed in Teflon® vessels and were stored in the form of water suspensions in autoclaves at 100°C for 24 hours.

Thus, the hydrothermal technique provides unique opportunities for a preparative chemist to obtain a large variety of hydroxides, hydroxyl carbonates, hydroxylchlorides, etc., of various metals.

### 9.4 HYDROTHERMAL SYNTHESIS OF SELECTED OXIDES

Oxides form one of the largest groups of inorganic compounds both in nature and in the laboratory. The hydrothermal technique is one of the most popular techniques for growing these high-temperature oxides, complex oxides and low-temperature modifications of the oxides. The work on the hydrothermal synthesis of oxides began during the 19th century with quartz in 1845.[44] Followed by this, large-scale research activity began during the 1890s, on corundum and other related high-temperature oxides.[45][46] Today, we find a large number of oxides obtained by the hydrothermal method: TiO$_2$, ZrO$_2$, HfO$_2$, Cu$_2$O, BeO, Bi$_2$O$_3$, In$_2$O$_3$, Al$_2$O$_3$, ZnO, Fe$_2$O$_3$, to mention a few, and a great variety of mixed oxides. Some of these carry great significance as synthetic gemstones, and some as technological materials. Here, we describe the hydrothermal growth of selected oxides of both gemstone and technological grades.

#### 9.4.1 Cu$_2$O (Cuprite)

The growth of cuprite monocrystals under hydrothermal conditions can be carried out using LiOH, NaOH, KOH in aqueous solutions of alkali ammonium halogenides. Kuzmina and Kaidukov (1977) have worked out a detailed technology of hydrothermal synthesis of cuprite, and the solubility of cuprite can be written as follows:[47]

\[
\text{Eq. (5)} \quad \text{Cu}_2\text{O} + (2a - 2) \text{OH}^{-} \rightarrow 2\text{CuOa}^{(2a-1)^{-}} + (a - 1) \text{H}_2\text{O}
\]

The solubility of hemioxide of cuprite under high-pressure-temperature conditions is less stable with respect to supersaturation, and with a slight variation in the temperature gradient, spontaneous crystallization of cuprite takes place such that the growth of cuprite crystals become difficult.
Cuprite crystal growth is carried in autoclaves with copper or silver linings. The growth temperature is 250–450°C, \( \Delta T = 25–75^\circ \), %fill 70 to 80%. For chloride solutions, Teflon® liners have been used and the temperature was maintained at \( T = 300^\circ \)C and \( \Delta T = 20–45^\circ \), and the pH varied from 5.0 to 5.5. The crystals obtained are 4–5 mm in size with ruby-red color having octahedral or often dodecahedral cover.

### 9.4.2 BeO (Bromelite)

Extremely high toxicity of beryllium makes the crystal growth of beryllium-bearing compounds very difficult. Therefore, the hydrothermal method becomes most useful in this regard. The first attempt to grow bromelite was made by Hartmann (1962).\[48\] Seeded growth of bromelite was carried out using a 5 mm BeO crystal oriented along [1\( \overline{1} \)0\( \overline{1} \)] and [1\( \overline{1} \)0\( \overline{1} \)]. The average growth rate was \(~ 0.07\) mm/day. The crystallization was carried out at 500–530°C using NaOH solutions.

The autoclaves are usually provided with copper or silver lining though there are several other lining materials. The experimental conditions are as follows:

- **Mineralizer**: 25wt% NaOH
- **Nutrient**: beryllium oxide
- **Fill %**: 80%
- **Crystallization temperature**: 450°C
- **\( \Delta T \)**: 20–50°C

Under the above conditions, colorless hexagonal crystals of size 3–4 mm with the basic pinacoidal, pyramidal and prismatic forms are formed.

### 9.4.3 Zinc Oxide

Zinc oxide is well-known as \( n \)-type semiconductor due to the excess of Zn atoms in the compound. Because of its high electromechanical coupling constant, zinc oxide appears to be the best material for devices utilizing the piezoelectric interaction between acoustic waves and electronic current. Zincite crystals may be grown by different methods: from gas phase (it produces needles of ZnO), from high-temperature
solution using PbF$_2$ (it produces plate-like crystals), and hydrothermally. It is interesting to note that the properties of crystals grown by the first two methods are technologically unsatisfactory owing to the imperfections in the crystal, and to unsuitable habits. Therefore, the most promising method of producing isometric zinc oxide crystals of good quality is the hydrothermal method \cite{49}. Hence, the process of crystallization represents an important technique for many applications. In this respect, understanding, controlling, and optimizing crystal morphology is of fundamental importance in those fields where an incorrectly defined crystal morphology may have an impact upon a number of important technological applications. Therefore, the hydrothermal technique is found to be the most suitable one for the growth of ZnO crystals. Seeded crystal growth of zincite has been carried out using NaOH and KOH solutions and, similarly, aqueous solutions of chlorides \cite{50}–\cite{54}. The most useful solvent is 2–10M KOH, in which the growth takes place within a wide temperature interval 200–500°C and $P = 150–600$ atm. Lobachev et al. (1982) have studied the solubility of zincite in detail. The solubility is less dependent upon the temperature when the concentration of the solution is < 3M, but for higher concentrations, it is distinct. Figure 9.6 shows the solubility of zincite in KOH solution. With a raise in the concentration of KOH, the solubility of zincite in KOH solution increases nonlinearly, but with a raise in the concentration of KOH at lower temperature (< 200°C), it becomes linear.

Figure 9.6. Solubility of zincite in KOH solution \cite{50}
In the growth of zincite, the use of alkalis sometimes leads to the formation of hydrogen arising as a result of the oxidation of the autoclave material. The amount of hydrogen formed depends greatly on the temperature, the concentration of the alkali, and the duration of the experiment. In fact, the dissolution of the crystals, the transport processes, and crystallization in turn, depend greatly on the redox potential of the medium. Sakagami (1990) has obtained zincite crystals of high purity by the hydrothermal method under a partial pressure of oxygen, using platinum-lined autoclaves and ultra-pure reagents.\[55]\ The growth conditions are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temperature</td>
<td>370–400°C</td>
</tr>
<tr>
<td>Temperature difference</td>
<td>10–15°C</td>
</tr>
<tr>
<td>Total pressure</td>
<td>700–1000 kg/cm</td>
</tr>
<tr>
<td>Partial pressure</td>
<td>10–30 kg/cm</td>
</tr>
<tr>
<td>Solvent</td>
<td>KOH 3.0M + LiOH 1.5M</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>H$_2$O$_2$ 0.1M–0.3M</td>
</tr>
<tr>
<td>Nutrient</td>
<td>ZnO sinter</td>
</tr>
<tr>
<td>Lining tube</td>
<td>Point (0.3 mm thickness)</td>
</tr>
<tr>
<td>Growth run</td>
<td>15–20 days/run</td>
</tr>
</tbody>
</table>

Figure 9.7 shows high purity crystals of zincite obtained at a growth rate of 0.2 mm/day in a direction normal to a prismatic face (1010). The degree of coloration depends upon the growth conditions, for example, solutions containing a H$_2$O$_2$ oxidizer and without an oxidizer. The author has used the coulometric technique to detect a small deviation in the stoichiometric constituent towards Zn$_{1+x}$O. The concentration of excess Zn in the crystals grown under excess partial pressures of oxygen decreased to the minimum of 0.8 ppm, and their resistivity increased to about $10^8$ Ωm. Thus, the composition of the solution in which the zincite crystallizes changes the habit and properties of the developing crystals. In KOH solutions, ZnO crystals or prismatic habit, drawn out sharply along the ‘c’ axis, are formed in caustic soda solutions. The crystals are more isometric in LiOH solutions. The growth rate of the monohedral face is very slow, while that of the pyramid face is commensurable with or slightly exceeds that of the prism, and the crystals assume a tabular form. The presence of F$^-$ ions in the solution increases the growth rate of the monohedral (0001) face. If the solution contains iron, characteristic zincite twins grow along the face of
the monohedron. In aqueous ammonium chloride solutions (1–7 wt%), recrystallization of zincite takes place at 450°C. The crystal habit varies with the concentration of the solution. In highly concentrated solutions, hexagonal platelets form. Hence, in order to obtain good crystals of zincite, NaOH and KOH solutions are used. The resistance of zincite crystals grown in alkali solutions containing lithium ions is small: $10^1$–$10^2$ Ωcm. Annealing in air or oxygen increases the resistance of the samples to $10^5$–$10^8$ Ωcm. This is due to the diffusion of the Li ions, and to the motion of the hyper-stoichiometric proportion of zinc to the surface of the crystal faces, with its subsequent oxidation to zinc oxide.

![High purity crystals of zincite obtained at a growth rate of 0.2 mm/day.](image)

**Figure 9.7.** High purity crystals of zincite obtained at a growth rate of 0.2 mm/day. (55)

Zincite crystals obtained under hydrothermal conditions are normally activated by Mn$^{2+}$ and Ni$^{2+}$, which emit red and green radiation. However, the resistance of the crystals remains unchanged. Similarly, the Mn$^{2+}$ and Ni$^{2+}$ ions also have no appreciable effect on the kinetics of the crystallization of zincite.

Wang et al. (1997) has carried out a systematic investigation of zincite crystals and their morphology through a crystal chemical approach to obtain a desirable morphology. Also, they have explained the effects of the additive OH$^-$ on the crystal morphology of ZnO crystallites. ZnO microcrystallites are very important having wide application in ceramics, coatings, and electronic devices. Thus, hydrothermal zincite crystals have great device potential.
9.4.4 Hydrothermal Growth of Corundum

The hydrothermal synthesis of corundum began during the 1890s. Corundum is stable under hydrothermal conditions at \( T > 400^\circ\text{C} \)\(^{[59][60]} \) and is soluble in alkali and carbonate solutions. According to Laudise and Parker (1974), corundum shows a lower temperature coefficient of solubility in alkaline solutions and that is the reason for the unsuccessful growth of corundum in these solutions.\(^{[61]} \) Although, hydrothermally grown corundum is commercially available at present, as gemstones it has not been reported. The hydrothermal growth of corundum is achieved using a metastable-phase technique because of its very low solubility. Gibbsite \((\text{Al(OH)}_3)\) is used as a nutrient, \( \alpha-\text{Al}_2\text{O}_3 \) as a seed, and an alkaline solution as a solvent. A more rapid growth rate is obtained in KOH or \( \text{K}_2\text{CO}_3 \) solution than in NaOH or \( \text{Na}_2\text{CO}_3 \) solution. The solubility is lower in KOH or \( \text{K}_2\text{CO}_3 \), but the interaction between the impurity absorbed beforehand onto the crystal surface and \( \text{K}^+ \) ion existing in the solution, acts as a factor to augment the growth rate. The lower the pH level in the solution, the thicker the growth layer along the \( c \)-axis. The growth of corundum in extremely low pH 6N HCl has been reported. In this case, the nutrient is dissolved at the lower temperature side and is deposited on the seed crystal at the higher temperature side, because the enthalpy in the \( \alpha-\text{Al}_2\text{O}_3-\text{HCl} \) reaction is negative. Isothermal studies of the system \( \text{Al}_2\text{O}_3-\text{H}_2\text{O} \) have been carried out by many workers and have shown that corundum could be formed from diaspore, boehmite, or gibbsite \textit{in situ} at temperatures > 450°C. The pressure varied from 15,000 to 30,000 psi. Figure 9.8 shows the phase relations in \( \text{Al}_2\text{O}_3 \) systems.\(^{[61]} \) Kashkurov et al. (1968) have studied the growth of large corundum crystals at pressures up to 2000 atm and at temperatures up to 550°C in alkali solutions of various concentrations. Crystals weighing up to 1 kg were prepared by the hydrothermal technique, and the imperfect state of these crystals was apparently associated with internal stresses and the mosaic structure of seed crystals which were prepared by Verneuil technique.\(^{[62]} \) Rumyanetsev et al. (1972) have shown that among alkali and carbonate solutions, the alkali solutions dissolve corundum and form aluminates.\(^{[63]} \)

\[
\text{Eq. (6)} \quad \text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{Na}[\text{Al(OH)}_2] + 4\text{OH}^- 
\]
In the absence of carbonate ions, CO$_3^{2-}$, the aluminate ions are always stable and the reaction becomes irreversible and, at the same time, with the use of carbonate solutions, the reaction becomes reversible. In fact, this is a characteristic feature of lower concentrations of sodium bicarbonate. At higher concentrations of solutions, usually, the heavier phases appear. In aqueous solutions of K$_2$CO$_3$ and Pb$_2$CO$_3$, the heavy phase does not appear, therefore, the experimenters emphasize the corundum growth in such solutions. Figure 9.9 shows the dependence of the solubility of corundum on temperature; and Fig. 9.10 shows the dependence of the growth rate of different faces on the temperature. With a raise in temperature, the growth rate nonlinearly increases within the temperature interval 400–500°C. Good quality corundum crystals were grown on the seeds oriented along the face (122) and were obtained from the melt. The growth was carried out in 4M K$_2$CO$_3$ solution at 480°C.
pressure of 1330 atm, fill 85\%, \Delta T = 30^\circ\text{C}, \text{ and colorless and transparent crystals with (211), (311) and (111) faces were obtained. Thomas (1996) has studied the influence of KOH/CO}_2\text{ ratio in alkaline-bicarbonate solutions on the growth rate of corundum crystals under hydrothermal conditions. It has been shown that the concentration of CO}_2\text{ in the system has a main influence on the growth rate of corundum crystals; as for KOH content in the bicarbonate solutions, it influences growth velocity with only a small concentration of the alkaline component. A mechanism for aluminum transfer with the growth of corundum crystals in the carbonate and bicarbonate solutions has been discussed.}[64] The corundum of hydrothermal origin is used both as gemstone and technological material.

![Figure 9.9. Dependence of solubility of corundum.[63]](image)

![Figure 9.10. Dependence of the growth rate of different faces and the temperature.[63]](image)
The hydrothermal technique is useful for obtaining large crystals of sapphire and ruby. The corundum modifications of Al$_2$O$_3$, which are relatively strain free, can be prepared at moderate temperature conditions and without the excessive gradients characteristic of flame fusion and melt techniques. These are the gemstone varieties of corundum and named according to their colors: sapphire blue and ruby red. Probably sapphire is the second material after quartz to be grown in any size by hydrothermal methods. Similarly, large ruby crystals can be grown using carbonate solutions. The solubility of sapphire and ruby is the same as that of corundum and it increases with temperature. Oxides of chromium and iron, when taken in the nutrient along with Na$_2$CO$_3$ solution, more strongly influence the crystallization than when taken with K$_2$CO$_3$ solution. However, when the concentration of these components in the nutrient is higher than 1.6% in 10% Na$_2$CO$_3$ solution, crystals practically do not grow. Kuznetsov and Shternberg (1967) have investigated the crystallization of ruby under hydrothermal conditions by three methods: recrystallization of aluminum oxide in solutions containing chromium; joint recrystallization of Al$_2$O$_3$ and Cr$_2$O$_3$, which are placed in the autoclave as separate components; and finally, recrystallization of ruby crystals having a given chromic oxide concentration. The last method makes possible uniform and controlled introduction of the impurity into the solution and the growing crystal throughout the experiment. Figure 9.11 shows the growth rate of the (101–1) face versus Cr$_2$O$_3$ concentration in the initial charge; 10% Na$_2$CO$_3$ solution at 550°C, autoclave 60% filled. These authors conclude that in carbonate and bicarbonate solutions, chromic oxide, and aluminum oxide have substantially different solubilities in carbonate solutions and different rates of dissolution. Also, the effect of solution redox potential on the transport of chromic oxide under hydrothermal conditions has been studied by these authors. Monchamp et al. (1967) have carried out very large-scale growth of sapphire and ruby with considerable success. Figure 9.12 shows hydrothermally grown ruby crystal. Green crystals containing iron have been grown by carrying out the crystallization in the welded liners directly, and colorless crystals which were essentially pure have been prepared by the use of a silver tube. The overall features are similar to the growth of corundum crystals.
Figure 9.11. Growth rate of (1011) face versus Cr$_2$O$_3$ concentration in the initial charge.$^{[65]}$

Figure 9.12. Hydrothermally grown ruby crystals.$^{[68]}$ (Courtesy of V. S. Balitskii.)
9.4.5 Hydrothermal Growth of Oxides of Ti, Zr and Hf

The oxides of titanium, zirconium, and hafnium belong to a group of chemically stable compounds with high melting points. These properties make them very important technological materials, but at the same time restrict the possibility of growing them in the form of single crystals. Among these three compounds, TiO$_2$ melts easily (1850°C) and can be grown by direct melting (Verneuil method), but analogous methods have not yet found successful practical application for ZrO$_2$ and HfO$_2$, since the melting points are rather high, 2700°C and 2780°C respectively. Hence, Li$_2$MoO$_4$, PbF$_2$, Na$_2$B$_2$O$_4$ fluxes are used to grow these crystals, as their high melting points make them difficult to grow directly from the melt. Although the crystallization of rutile by the Verneuil method is frequently employed, the method often yields crystals of a nonstoichiometric nature. Kuznetsov (1973) has reviewed the growth of oxides of titanium subgroup metals in detail.[69] Anikin et al. (1965) have obtained TiO$_2$ at 550°C and 1000 atm.[70] Subsequently, Harville and Roy (1967) have obtained TiO$_2$ crystals in H$_2$SO$_4$ solutions at 700°C and 1000–4000 atm. However, the growth rate was very low.[71] The commonly used solvents are solutions of alkalis, lithium, potassium, sodium, and ammonium carbonates and bicarbonates, sodium sulfide, lithium, potassium and ammonium chlorides, sulfates (Na$_2$SO$_4$, K$_2$SO$_4$), borax, boric acid, and fluorides (KF, NaF, NH$_4$F). The concentrations of the solutions were 5–40%.

TiO$_2$. Kuznetsov and his group have worked out the growth technology of TiO$_2$ (rutile phase) under hydrothermal conditions[69][72][73] using 7–10% KF or NaF and 5–10% NH$_4$F solutions at temperatures over 500–550°C and pressures of 500–800 atm. The amount of material transported increases with increasing temperature of the experiment. Crystals are prismatic with dark-brown or black color. When a small amount of KClO$_3$ is added to the nutrient, crystals become light green in color. Rutile synthesized by the hydrothermal method has properties closer to the natural rutile. In pure water and aqueous solutions of NaOH or Na$_2$CO$_3$ at temperatures below 350–400°C, the anatase phase of TiO$_2$ crystallizes and, at temperatures further down, the brookite phase crystallizes.[73]

A rutile crystal grown by Verneuil method was used as a seed and experiments were carried out at a solubility zone temperature 550–600°C, with respective autoclave filling coefficients of 0.6–0.5 and $T = 20–35°C$.[73] Under these conditions the growth rate of the (100) and (110) faces was 0.15–0.21 mm/day in the five-day experiments. Typical conditions for
crystallization were 570°C, autoclave filling coefficient = 0.6, $\Delta T = 25^\circ C$. However, the given directions (100) and (110) are not directions of rapid growth. Judging by the morphology of the spontaneous rutile crystals (they often have a typical long-prismatic form), the growth rate along (001) should be higher.

**ZrO$_2$ (Baddeleyite).** Kuznetsov (1973) was the first to synthesize ZrO$_2$ crystals under hydrothermal conditions using fluoride solutions of NaF, or KF and NH$_4$F with concentrations 7–10% at temperatures of 520–690°C. In KF solutions, ZrO$_2$ is transported only at temperatures over 600°C, and small crystals of 0.5 mm size are formed in the upper zone of the autoclave. Below 600°C, all that happens is that the original material is made coarser, and lamellar crystals up to 0.3 mm in size are formed in the lower zone of the autoclave. In NH$_4$F solution, there occurs an intensive recrystallization of ZrO$_2$ at relatively low temperatures. However, there are some practical difficulties in the growth of ZrO$_2$ due to the retrograde solubility in NH$_4$F solutions. In order to simplify the problem, in a furnace with a horizontal autoclave, a “hot” zone was created at the obturator. By this means, ZrO$_2$ crystals in the form of thin plates 2.5 × 2.5 × 0.5 mm with (001), (010) and (110) faces were obtained. Increase in the temperature gradient raises the growth rate and the crystals become thicker and form twinning. Growth rate is maximum in the “c” direction, minimum in the “a” direction, and slower in the “b” direction. The growth rate of the (100) face is roughly ten times lower than that of the (001). The basic properties of this synthetic ZrO$_2$ are closer to the mineral baddeleyite. Figure 9.13 shows a photograph of ZrO$_2$ crystals grown under hydrothermal conditions.

![ZrO$_2$ crystals grown under hydrothermal conditions](image_url)
HfO₂. According to Kuznetsov (1968), the growth of HfO₂ does not differ much from that of ZrO₂. The crystallization of HfO₂ takes place at a higher temperature in KF and NaF solutions and at still higher temperatures in NH₄F solution (700°C). Again, the major disadvantage is the higher temperature of crystallization and retrograde solubility. Hence, in this case also, a horizontally disposed autoclave was used by Kuznetsov and his group. The autoclave had a transverse baffle in which the orifice area was ~15% of the internal cross sectional area. Crystals up to 2 × 2 × 0.5 mm of HfO₂ (Fig. 9.14) were obtained.

![Figure 9.14. HfO₂ crystals](https://example.com/hfo2_crystals.png) (Courtesy of V. A. Kuznetsov.)

9.5 HYDROTHERMAL GROWTH OF TELLURIUM DIOXIDE

Tellurium dioxide has two modifications: tetragonal (paratellurite) and orthorhombic (tellurite). Among these two, the paratellurite is of great interest for solid state physicists, because of its valuable piezoelectric and acousto-optical properties. In particular, paratellurite crystals may be used in acousto-optical modulators of light deflectors and delay lines. At present, there are several methods of growing these crystals. The most popular is the Czochralski method but, in this method, the growth temperature is high and there are strong temperature gradients in the growth region. This, together with high vapor pressure of tellurium dioxide, often results in the production of defected and stressed crystals. In addition, the method is rather cumbersome and only about 20% of crystals produced have acceptable quality.
The hydrothermal method of crystallization of paratellurite started almost at the same time as that of the Czochralski method. However, the effects of various physical and chemical parameters on the growth of paratellurite crystals were not properly studied. This technology is not advantageous because of its poor reproducibility and poor quality of crystals. The possibility of obtaining spontaneous paratellurite monocrystals from solutions of hydrohalogenic acids was demonstrated in Ref. 64. It was found that the mass crystallization decreases in the following sequence: HCl > HBr > HI > HF, while all other parameters are the same.

The experiments done in platinum lined autoclaves showed that platinum dissolves in hydrohalogenide complexes, hence, the process of dissolution of TeO₂ in the acid deteriorates and goes out of control. Thus, effective usage of hydrothermal technology of paratellurite could not be developed owing to the difficulties in observing and controlling the parameters which determine the crystallization of α-TeO₂ in platinum-lined steel autoclaves.

Popolitov et al. (1975) have studied the solubility of paratellurite in detail in hydrochloric acid, which is an effective solvent for the recrystallization of TeO₂. Figure 9.15 shows the dependence of solubility of tellurium dioxide and HCl concentration measured by titration with sodium hydroxide. The starting material used was monocrystals of paratellurite obtained through spontaneous crystallization from water solutions of HCl.

Figure 9.15. Dependence of solubility of tellurium dioxide and HCl concentration.\textsuperscript{77}
The hydrothermal growth of monocrystals on seeds is known to include the following stages: dissolution of solid substance, transport of dissolved materials to the growth region, and the growth of seed crystals. To reveal the mechanism of transport, it is of great importance to use the data on solubility of paratelluride in HCl solutions and to consider the possible mechanism of transport from the dissolution region to the growth region in the process of $\alpha$-TeO$_2$ growth on the seed.

The synthesis of paratellurite with 100% output occurs in aqueous solutions of nitric acid with concentrations up to 25% at temperatures of 260–340°C and pressures of 50–370 atm.\[74] Element tellurium serves as the nutrient, so that the synthesis reaction occurs as follows:

Eq. (7) \[ 3\text{Te} + 4\text{HNO}_3 \rightarrow 3\text{TeO}_2 \text{ (solid)} + 2\text{H}_2\text{O} + 4\text{NO} \uparrow \]

With further rise in the concentration of aqueous nitric acid solution (>25%), there occurs the oxidation of the tellurium with the formation of crystals of telluric acid:

Eq. (8) \[ \text{Te} + 6\text{HNO}_3 \rightarrow \text{H}_2\text{TeO}_4 \text{ (solid)} + 6\text{NO}_2 + 2\text{H}_2\text{O} \]

The morphology of paratellurite crystals is very interesting. The crystals grown in hydrochloric acid solutions exhibit more complex forms than the crystals obtained in nitric acid solutions. The paratellurite monocrystals grow in the form of a tetragonal prism (110) and tetragonal dipyramids (101) and (102). The growth forms of tellurium oxychloride monocrystals are pinacoids (001) and (010), rhombic prisms (110) and (130), and rhombic dipyramids (111), (112), (113), and (114). Figure 9.16 shows the habits of (a) tellurium dioxide, and (b) tellurium oxychloride crystals.

Popolitov and his group have studied, in detail, the kinetics of crystallization of paratellurite under hydrothermal conditions with reference to the mass transport, temperature gradient, solution concentration, growth rate and so on.\[77][78] On the basis of the kinetic study of growth conditions for $\alpha$-TeO$_2$ crystals, it was found that the growth rate in the homogeneous solution is limited by diffusion mass transport of the dissolved substance towards the growing faces, while in the binary phase, the surface processes are limited. A method for the optimal growth of the uniform $\alpha$-TeO$_2$ monocrystals was developed wherein the crystals are grown on seeds and in 3.65 wt% water solution of HCl at 150–200°C.
Acoustic characteristics of \( \alpha \)-TeO\(_2\) monocrystals obtained by the hydrothermal method are similar to those of Czochralski grown crystals. A reader can find more information in Ref. 79.

![Figure 9.16. Habits of (a) tellurium dioxides and (b) tellurium oxychloride crystals.][77]

### 9.6 HYDROTHERMAL SYNTHESIS OF TiO\(_2\) AND RELATED OXIDE POWDERS

There is a growing interest in the application of oxide semiconductors as catalyst supporters, photocatalysts, oxidation catalysts, and electrocatalysts for carrying out chemical transformations of organic and inorganic compounds.\[^{[80]}\]–\[^{[82]}\] Fe\(_3\)O\(_4\) powders with a spinel structure have potential applications for ferrofluid magnetic refrigeration, bioprocessing, and information storage.\[^{[83]}\] Several other oxides like SnO\(_2\) are used as gas sensors,\[^{[84]}\] and \( \alpha \)-MnO\(_2\) as an adsorbent.\[^{[85]}\] Among these especially, TiO\(_2\) is the most important material being studied extensively in the last few years owing to its unique properties. TiO\(_2\) shows maximum light scattering with virtually no absorption. It is non-toxic and chemically
inert. This has been employed extensively in studies of heterogeneous photocatalysis and has been accepted as one of the best photocatalysts for the degradation of environmental contaminants. The process involves the absorption of a photon by TiO$_2$, leading to the promotion of an electron from the valence band to the conduction band and thus produces an electron hole. The electron in the conduction band is then removed by reacting with O$_2$ in the outer system. The hole in the valence band can react with OH$^-$ or H$_2$O species, which are adsorbed on the surface of the TiO$_2$ to give the hydroxyl radical. This hydroxyl radical initiates the photocatalytic oxidation, a pollution control technology or detoxification technology$^{[86]}$ which destroys the organic chemical contaminants in air, water, and soil. It can be used to treat the polluted water (both surface and ground water, similarly waste and drinking water) and soil. The technique can be used as an industrial pollution management technique for cleaning up gaseous and aqueous waste streams containing organic compounds. The photocatalytic activity of TiO$_2$ depends upon its crystal structure (anatase, or rutile), surface area, size distribution, porosity, and presence of dopants, surface hydroxyl group density, etc. These factors influence directly on the production of electron-hole pairs, the surface adsorption and desorption process and the redox process.

There are several ways of preparing TiO$_2$ particles.$^{[87]}$–$^{[90]}$ The hydrothermal method has many advantages like producing a highly homogeneous crystalline product, which can be obtained directly at relatively lower reaction temperature (<150°C). Its most important feature is that it favors a decrease in agglomeration between particles, narrow particle size distributions, phase homogeneity, and controlled particle morphology. It also offers the uniform composition, purity of the product, monodispersed particles, control over the shape and size of the particles, and so on. The hydrothermal technique has been found to be one of the best techniques to prepare TiO$_2$ particles of desired size and shape with homogeneity in composition and a high degree of crystallinity. Hence, the authors have carried out the synthesis of TiO$_2$ under hydrothermal conditions and have used the material in the degradation of organic compounds.

It is well known that several organic pollutants present in industrial waste waters, phenol, nitrophenol isomers and their derivatives, aromatic hydrocarbons, cyanide, sulfites, and so on, have been completely removed by using this TiO$_2$ based heterogeneous photocatalysis. Several authors have studied in detail the mild hydrothermal synthesis of TiO$_2$ particles and the influence of various parameters like temperature,
The synthesis of TiO$_2$ is usually carried out in small autoclaves of Morey type, provided with Teflon$^\text{®}$ liners. The conditions selected for the synthesis of TiO$_2$ particles are: $T = < 200^\circ\text{C}$, $P < 100$ bars. Such pressure-temperature conditions facilitate the use of autoclaves of simple design provided with Teflon$^\text{®}$ liners. The use of Teflon$^\text{®}$ liners has helped to obtain pure and homogeneous TiO$_2$ particles. Though the experimental temperature was low ~ 150$^\circ$C, TiO$_2$ particles with a high degree of crystallinity and the desired size and shape could be achieved through a systematic understanding of the hydrothermal chemistry of the media. Here it is appropriate to mention that the size of the titania particles is a most critical factor for the performance of the material in the photocatalytic activity, and the monodispersed nanoparticles are the most suitable ones. It has been shown that the particle size is a crucial factor in the dynamics of the electron/hole recombination process, which offsets the benefits from the ultrahigh surface area of nanocrystalline TiO$_2$. The dominant e$^-$/h$^+$ recombination pathway may be different for TiO$_2$. Different particle size regimes have been established for improving the photocatalytic efficiencies of different systems.$^{[91]}$

The starting materials such as that of TiO$_2$ and the solvent with a definite molarity (1.5 to 4.0 m) were taken in a Teflon$^\text{®}$ liner. The internal pressure was maintained below 100 bars through percent fill in the liners. The starting mixture was stirred thoroughly to obtain a homogeneous and relatively viscous solution, which was later kept inside an autoclave and heated at 150$^\circ$C for about 40–48 hours. Several solvents like NaOH, KOH, HCl, HNO$_3$, HCOOH and H$_2$SO$_4$ were treated as mineralizers and it was found that HNO$_3$ is a better mineralizer for obtaining monodispersed nanoparticles of titania with homogeneous composition under the present experimental conditions.$^{[82]}$ The authors have used different starting charges such as reagent grade anatase, sintered anatase (at about 800 to 900$^\circ$C for 10 hours), TiCl$_4$ and titanium gel. In each case, the resultant product was TiO$_2$, however, with different ratios of rutile and anatase depending upon the charge, as confirmed from the x-ray powder diffraction studies. Though the rutile phase was more dominant in the resultant product, the presence of a small amount of anatase persisted except when the experimental temperature was approximately 200$^\circ$C. When sintered anatase or titanium gel was used as charge, it yielded better results, for example, the resultant
product contained more or less uniformly sized or monodispersed particles with a high degree of crystallinity, and interestingly, the rutile phase was formed as a prominent phase with a better yield. Better results, in this sense, meant good photocatalytic activity because of the monodispersed particles with a high degree of crystallinity. Similarly, the authors have tried TiCl₄ as charge, and the resultant product contained both anatase and rutile. The formation of a single phase required the proper selection of pH of the media and crystallization temperature. The present authors have carried out the TiO₂ synthesis within a wide range of pH values of the media. When the pH of the medium was low (pH = 1 to 2) only rutile phase was formed. When the pH was kept even lower, i.e., in the negative range, the product contained a small amount of anatase also. As the pH of the medium was increased, the product contained essentially anatase with very little rutile. Thus, with the addition of KOH or NaOH, the formation of anatase phase was favored. With a further increase in the pH, i.e., beyond twelve, in the present experimental temperature, only an amorphous material was obtained. Raising the temperature results in the formation of alkali titanates. Table 9.2 gives the results of the mild hydrothermal experimental preparation of ultrafine particles of TiO₂. Thus, it is necessary to maintain a proper acidity in the system in order to obtain a homogeneous rutile phase. Similarly, control over the temperature, time, and pH of the medium helps in the preparation of a desired particle size and shape. When the reaction temperature and time were increased, it resulted in the formation of faceted grains of bigger size. Figure 9.17a and b shows the representative photographs of TiO₂ particles prepared under hydrothermal conditions. The following experimental conditions were maintained for the preparation of ultrafine rutile particles of TiO₂:

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>pre-heated anatase phase or Ti gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>150°C</td>
</tr>
<tr>
<td>Duration</td>
<td>40 hours</td>
</tr>
<tr>
<td>pH</td>
<td>2</td>
</tr>
<tr>
<td>Fill %</td>
<td>60%</td>
</tr>
<tr>
<td>Mineralizer</td>
<td>1.5 M HCl</td>
</tr>
</tbody>
</table>
### Table 9.2. Hydrothermal Experimental Conditions of the Preparation of TiO₂ Ultrafine Particles

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Nutrient</th>
<th>Solvent</th>
<th>% Fill</th>
<th>PH</th>
<th>T °C</th>
<th>Time Hours</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>TiO₂ – 2 gm WO₃ – 0.1 gm</td>
<td>1.5M HCl</td>
<td>60</td>
<td>2</td>
<td>150</td>
<td>40</td>
<td>Rutile &amp; anatase ultrafine particles</td>
</tr>
<tr>
<td>2.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm</td>
<td>1.5M HNO₃</td>
<td>65</td>
<td>1.8</td>
<td>150</td>
<td>45</td>
<td>Anatase &amp; rutile fine particles</td>
</tr>
<tr>
<td>3.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm</td>
<td>1.5M HCOOH</td>
<td>60</td>
<td>1.9</td>
<td>160</td>
<td>40</td>
<td>Rutile &amp; anatase fine particles</td>
</tr>
<tr>
<td>4.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm</td>
<td>1.5M H₂SO₄</td>
<td>55</td>
<td>2.0</td>
<td>160</td>
<td>40</td>
<td>Rutile &amp; anatase ultrafine particles</td>
</tr>
<tr>
<td>5.</td>
<td>TiO₂ – 2 gm WO₃ – 0.1 gm</td>
<td>1.5M HCl + 1.5M HNO₃</td>
<td>50</td>
<td>1.4</td>
<td>150</td>
<td>48</td>
<td>Anatase &amp; rutile</td>
</tr>
<tr>
<td>6.</td>
<td>TiO₂ – 2 gm WO₃ – 0.1 gm</td>
<td>1.5M HCl + 1.5M HCOOH</td>
<td>60</td>
<td>1.3</td>
<td>160</td>
<td>48</td>
<td>Anatase &amp; rutile</td>
</tr>
<tr>
<td>7.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm</td>
<td>1.5M HCl + 1.5M H₂SO₄</td>
<td>60</td>
<td>1.2</td>
<td>150</td>
<td>40</td>
<td>Anatase &amp; rutile particles</td>
</tr>
<tr>
<td>8.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm NaOH – 1 gm</td>
<td>1.5M HCl</td>
<td>65</td>
<td>2.8</td>
<td>150</td>
<td>40</td>
<td>Rutile &amp; anatase ultrafine particles</td>
</tr>
<tr>
<td>9.</td>
<td>TiO₂ – 2 gm WO₃ – 0.1 gm NaOH – 0.1 gm</td>
<td>1.5M HCl</td>
<td>60</td>
<td>3.4</td>
<td>150</td>
<td>48</td>
<td>Rutile &amp; anatase particles</td>
</tr>
<tr>
<td>10.</td>
<td>TiO₂ – 2 gm WO₃ – 0.1 gm NaOH – 3 gm</td>
<td>1.5M HCl</td>
<td>65</td>
<td>4.2</td>
<td>150</td>
<td>60</td>
<td>Na₂Ti₆O₁₃ Na₂Ti₃O₇ grains</td>
</tr>
<tr>
<td>11.</td>
<td>TiO₂ – 2 gm WO₃ – 0.1 gm NaOH – 2 gm</td>
<td>2.5M HCl</td>
<td>50</td>
<td>1.2</td>
<td>160</td>
<td>55</td>
<td>Anatase &amp; rutile particles</td>
</tr>
<tr>
<td>12.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm</td>
<td>4M HCl</td>
<td>55</td>
<td>0.8</td>
<td>150</td>
<td>40</td>
<td>Anatase &amp; rutile</td>
</tr>
<tr>
<td>13.</td>
<td>TiO₂ – 2 gm WO₃ – 0.3 gm NaOH – 6 gm</td>
<td>1.5M HCl</td>
<td>55</td>
<td>8.1</td>
<td>200</td>
<td>48</td>
<td>Na₂Ti₃O₇</td>
</tr>
</tbody>
</table>

*Cont’d.*
Table 9.2. (Cont’d.)

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Nutrient</th>
<th>Solvent</th>
<th>Fill %</th>
<th>PH</th>
<th>T °C</th>
<th>Time Hours</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.</td>
<td>TiO₂ –2 gm WO₃ – 0.3 gm ethanol – 0.1 wt%</td>
<td>1.5M HCl</td>
<td>60</td>
<td>2.8</td>
<td>150</td>
<td>40</td>
<td>TiO₂ ultrafine particles with a good yield</td>
</tr>
<tr>
<td>15.</td>
<td>TiO₂ –2 gm WO₃ – 0.3 gm urea – 0.1 wt%</td>
<td>1.5M HCl</td>
<td>60</td>
<td>2.7</td>
<td>150</td>
<td>40</td>
<td>TiO₂ ultrafine particles with a good yield</td>
</tr>
<tr>
<td>16.</td>
<td>TiO₂ –2 gm WO₃ – 0.3 gm tetrabutyl – ammonium 0.1 wt%</td>
<td>1.5M HCl</td>
<td>60</td>
<td>3.0</td>
<td>150</td>
<td>38</td>
<td>TiO₂ ultrafine particles With a good yield</td>
</tr>
<tr>
<td>17.</td>
<td>Titanium gel 2.5 gm WO₃ – 1.0 wt%</td>
<td>1.5M HCl</td>
<td>60</td>
<td>2.8</td>
<td>150</td>
<td>46</td>
<td>Ultrafine particles of rutile</td>
</tr>
<tr>
<td>18.</td>
<td>Sintered anatase – 2.0 gm WO₃ – 0.3 wt%</td>
<td>1.5M HCl</td>
<td>60</td>
<td>2.2</td>
<td>150</td>
<td>46</td>
<td>Ultrafine particles of rutile</td>
</tr>
</tbody>
</table>

Qian et al. (1993) have reported the preparation of ultrafine powders of TiO₂ by hydrothermal H₂O₂ oxidation starting from metallic Ti. This can be done in two steps: i) oxidation of Ti with an aqueous solution of H₂O₂ and ammonia to form a gel (TiO₂, H₂O), and ii) hydrothermal treatment of gel under various conditions. It is expressed as follows:
It is well known that the photocatalytic activity in TiO₂ increases with the addition of MoO₃, WO₃, or other active element. Therefore, the present authors have introduced WO₃ into the composition of TiO₂ from 5 and 10 wt% by adding the required amount of WO₃ into the nutrient (starting materials) and tested all the samples in the photocatalytic degradation of hydrocarbons. It is to be noted that the introduction of WO₃ up to 10 wt% did not change the homogeneity of the resultant product except for a slight increase in the cell volume. Also, the grain morphology and size did not alter significantly.

In some experiments, the authors have introduced a very small quantity of tetra butyl ammonium hydroxide or ethanol or urea. Addition of these organics enhances the crystallization kinetics greatly and also increases TiO₂ yield. However, the concentration of these organics was maintained at < 0.1 wt% as it alters the size and shape of the particles.

Figure 9.18 shows the TEM micrographs of TiO₂ powder prepared by hydrothermal treatment of gel. Chen et al. (1995) have prepared TiO₂ powders with different morphologies by an oxidation hydrothermal combination method. The effects of carboxymethyl cellulose sodium (CMC), HNO₃, Al³⁺ and K⁺ (F⁻) additives on the particle shape and crystalline structure are also discussed by these authors. They also studied the crystallization of TiO₂ in great detail, the influence of hydrothermal conditions, pH, reaction temperature, time and mineralizer. Figure 9.19 shows the TEM micrographs of the products with different mineralizers.

![Figure 9.18. TEM micrographs of TiO₂ powder.][89]
Figure 9.19. TEM micrographs of TiO$_2$ powder prepared by hydrothermal treatment of Gel: (a) in distilled water at 140°C for 12h, (b) in distilled water at 200°C for 12h, (c) in distilled water with 0.5wt% mineralizer of CMC at 140°C for 12h, (d) in 1.0N nitric acid solution at 140°C for 12h, (e) in 1.0M nitric solution at 140° for 24h, (f) in 1.5N nitric solution at 140°C for 12h, (g) in 1.0N nitric acid solution with mineralizer of 0.5wt% KF at 140°C for 12h, (h) in 1.0 N nitric acid solution with mineralizer of 0.5wt% KF at 140°C for 12h, and (i) in 1.0N nitric acid solution with mineralizer of 0.5wt% Al(NO$_3$)$_3$ at 140°C for 12h.$^{[80]}$ (Courtesy of the American Chemical Society, Washington, DC.)
Here, it is impossible to discuss the application of TiO$_2$ in great detail, because of the enormous amount of literature data available with reference to the photochemical transformations of organic and inorganic compounds, and the catalyst properties, for example, the honeycomb structured porous titania as an odor remover; improving the durability of automotive catalyst; using TiO$_2$ photocatalyst, the destruction of phenol in water,$^{[93]}$ and degradation of a large variety of trihalomethyl radicals.$^{[94]}$

Similarly, wastewater can also be treated.$^{[95]}$ Byrappa et al. (1999) have studied the photocatalytic degradation of HCCH, and DDT where complete mineralization occurs via the formation of benzophenone derivative Eq. (10).

\[
\text{Eq. (9)} \quad \text{HCCH} + 4\text{O}_2 + 5\text{H}_2\text{O} + ^\cdot\text{OH} \rightarrow 6\text{HCl} + 6\text{CO}_2 + 4\text{H}_2
\]

\[
\text{Eq. (10)} \quad \text{DDT} + 8\text{H}_2\text{O} + 10\text{O}_2 \rightarrow 14\text{O}_2 + 8\text{H}_2 + 5\text{HCl}
\]
In a typical experiment, solution of hexachlorocyclohexane (30 mg) with acetone (20 ml) taken in a flat bottomed flask was treated with 0.1N sodium carbonate (5 ml) and then diluted with distilled water until turbidity persisted. At this junction, one or two drops of acetone were added to clear the solution. To this test solution ~20mg of TiO₂ doped with WO₃ was added and kept in sunlight. Under similar conditions, a blank solution (without TiO₂) was also tested. TLC followed the progress of the reaction. At regular intervals, aliquots of the reaction mixture were removed from both the flasks and extracted into ether separately. It was then spotted on a TLC plate and developed in different solvent systems. The identification of spots was done by keeping the TLC plates in an iodine chamber. It was observed that, as the reaction time increased, the concentration of anthracene decreased and after 2–4 hrs, complete disappearance of HCCH occurred. Similar treatment was given to DDT, which took 5–6 hrs for complete mineralization.

Several authors[96]–[98] have carried out the preparation of magnetite powder. In the pure Fe₂O₃·H₂O system, α-Fe₂O₃ (hematite) is stable up to about 550°C. Above this temperature, up to 710°C, mixtures of α-Fe₂O₃ and Fe₃O₄ are stable. Runs above 710°C yield magnetite (Fe₃O₄) as the only stable phase. Viswanthiah et al. (1980) have conducted experiments in the temperature interval 100–600°C.[95] Traces of magnetite are found to be stable even at temperatures as low as 100°C. From 100 up to 200°C, iron formate (C₂H₂FeO₄·2H₂O) and hematite (α-Fe₂O₃) are the major phases along with traces of magnetite. HCOOH is used as the mineralizer, and it contributes to the formation of siderite phase also. Further, the liberation of carbon monoxide in the system creates a reducing environment, which promotes the stabilization of Fe₃O₄ rather than of Fe₂O₃. Thus, perfect octahedral crystals of magnetite are formed at 250°C. Figure 9.20 shows hydrothermally grown magnetite crystals, as well as aggregates.

Figure 9.20. Hydrothermally grown magnetite crystals. (Photo courtesy of Dr. J. A. K. Tareen.)
Although there are several methods of preparing crystalline iron oxide powders, hydrothermal and sol-gel techniques are supposed to be the most popular ones. Hirano and Somiya (1976) have obtained magnetite crystals under hydrothermal conditions in the presence of hydrogen. The hydrogen for the control of the reduced atmosphere was supplied by the reaction of charged metallic iron with water. The experiments were carried out at 550°C and 1000 kg/cm². As the concentration of hydrogen was increased, the (110) faces of magnetite were found to predominate over the (111) faces. The authors have used 10M NaOH as the solvent. No hematite formation was reported. Dendritic magnetite crystals were grown in 5M NH₄Cl solution at 500°C under 1000 kg/cm². Figure 9.21 shows the dendritic magnetite crystals grown in 5M NH₄Cl solution in 5.3M mole hydrogen.

Chen and Xu (1998) have prepared Fe₃O₄ particles of nanometer size hydrothermally from iron (II) 2-methoxyethoxides (Fe(OMOE)₂), using 2-methoxyethanol (MOE)-water mixed solvent as the medium. As in the TiO₂ preparation, here also the reaction conditions such as solvent, temperature, and time usually have important effects on the resultant products. These authors have shown that the particle size of Fe₃O₄ powders increase with prolonged reaction time.

In recent years, hydrothermal synthesis of magnetite in the presence or absence of organic chelating agents, oxidation of ferrous solutions using KNO₃, and solvothermal methods have become popular. The ability to direct the morphology of magnetite particles may be a key
feature in the development of new applications, particularly if other physical, chemical and electronic properties are retained. The formation of iron oxide phases is often influenced by the addition of secondary additives to aqueous systems containing either soluble or insoluble precursors of the iron oxides. There have been quite a few reports dealing with the influence of transition metals on the dissolution-precipitation reactions in which iron oxides can participate under hydrothermal conditions. McGarvey and Owen (1996) have obtained magnetite under hydrothermal conditions at 150°C and 175°C in the presence of hydrazine and copper (II) oxide. In the absence of CuO, octahedral crystals of magnetite corresponding to the literature data are found. In the presence of CuO, magnetite crystals with distorted morphology were prepared in which the crystal faces were absent, leaving a framework structure of corners and edges. (See Fig. 9.22.) Substitution of NiO, ZnO, or Ag₂O produced somewhat different results. Thus copper, as a result of having three accessible oxidation states [Cu(O), Cu⁺¹ and Cu⁺²] and rapid electron transfer between the species, is able to participate in a redox catalytic mechanism involving hydrazine to facilitate the reduction of hematite to magnetite as well as directing its morphology. Uchida et al. (1992) have prepared micaceous iron oxide by the oxidation of iron with pressurized oxygen in concentrated sodium hydroxide solution at elevated temperature. Thus, the preparation of iron oxide under hydrothermal conditions is an attractive field.

There are several other reports in the literature on hydrothermal synthesis of simple oxides like Mn₃O₄, PbO, VO₂, GeO₂, SnO₂, V₂O₃, R₂O₃, In₂O₃, Bi₂O₃, CdO, HgO, and so on.

Figure 9.22. Magnetite crystals with distorted morphology.
9.7 HYDROTHERMAL SYNTHESIS OF MIXED OXIDES

Mixed oxides form one of the most important modern materials. The group includes aluminates, garnets, spinel, metal oxides with complex structures, and so on. Especially in the last three to four years, the number of these complex oxides is increasing. Here, we discuss the hydrothermal synthesis of only some important complex oxides.

9.7.1 Hydrothermal Synthesis of Aluminates

The majority of the aluminates form in pure water at elevated temperatures (>500°C) and pressures (>1000 atm). The hydrothermal reaction involving divalent metals takes place through \( \text{MeO} + \text{Al}_2\text{O}_3 \rightarrow \text{MeAl}_2\text{O}_4 \).

Since pure water is used in the synthesis of these oxides, their solubility is very low, and to obtain 100% output, it is necessary to maintain the ratio of \( \text{MeO}/\text{Al}_2\text{O}_3 \) in the nutrient at 1:1—i.e., to the near stoichiometry. Aluminates crystallize as small crystals of < 0.1 mm. The aqueous solutions of NaOH are preferable in the synthesis, however, crystallization of aluminates of transitional metals (Fe, Co, Ni) takes place with the formation of corresponding oxides. Litvin and Popolitov (1984) have carried out the synthesis of aluminates of Ca, Be, Zn, Fe, Co and Ni under hydrothermal conditions.[101]

For alkaline earth metals (\( \text{MeO}/\text{Al}_2\text{O}_3 > 2:1 \)) the characteristic feature is the formation of hydrogarnets of type \( \text{Me}_3\text{Al}_2\text{O}_6\cdot6\text{H}_2\text{O} \). Crowley (1964) has carried out the synthesis of \( \text{Me}_3\text{Al}_2\text{O}_6\cdot6\text{H}_2\text{O} \) in the system \( \text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O} \), at temperatures less than 250°C and partial pressure of water 500–800 atm.[102]–[104] In pure water, 100% output is achieved at \( \text{MeO}/\text{Al}_2\text{O}_3 \) ratio in the nutrient equal to 3:1. The stoichiometry of the nutrient may be strongly inclined towards the surplus MeO while synthesizing in the aqueous solutions of NaOH. Moreover, in the synthesis of strontium hydrogarnet, it is shown that the monophase synthesis sharply increases in the highly concentrated solutions as shown in Fig. 9.23 for the system \( \text{SrO}\cdot\text{Al}_2\text{O}_3\cdot\text{NaOH}\cdot\text{H}_2\text{O} \) at 500°C.[105] The crystals are either cubic or rhombic dodecahedral in habit. Synthesis takes place at \( \text{CaO}/\text{Al}_2\text{O}_3 > 5:1 \) within the temperature interval 300–450°C.[105] Figure 9.24 shows the habit of the calcium aluminate crystals. Similarly, the strontium aluminates form.
Figure 9.23. Phase diagram for the system SrO-Al$_2$O$_3$-NaOH-H$_2$O at 500°C.\cite{105}

Figure 9.24. Habit of the calcium aluminate crystals.\cite{104}
In weakly concentrated solutions, new phases like $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, plate-like crystals of aluminates belonging to the rhombohedral symmetry with space group $\text{Pmm}a$ are obtained.

In the system $\text{Na}_2\text{O}(\text{K}_2\text{O})\cdot \text{Bi}_2\text{O}_3\cdot \text{Al}_2\text{O}_3\cdot \text{H}_2\text{O}$ bismuth tetra-alumininate, $\text{Bi}_4\text{Al}_4\text{O}_{13}$ crystals have been synthesized under hydrothermal conditions.$^{[103]}$ The crystallization occurs at higher concentration of $\text{Al}_2\text{O}_3$ in the nutrient in the order of 45–90 wt%. The pure phase occurs only when the molar ratio of $\text{Bi}_2\text{O}_3:\text{Al}_2\text{O}_3:\text{H}_2\text{O} = 0.8:0.05:1$, and with a rise in concentration of NaOH, the monophase synthesis reduces. This is connected with the structure becoming unstable with the rise in the concentration of NaOH. These crystals belong to the rhombic system with special group $\text{Pbam}$, and the crystals have (110) and (001) forms. However, the size of the crystals is $< 1.0$ mm.

9.7.2 Hydrothermal Synthesis of Antimonites and Antimonates

Oxides of trivalent antimony belong to the group of antimonates. Among hydrothermally synthesized rare earth penta-antimonites, $\text{R}_3\text{Sb}_5\text{O}_{12}$ and $\text{In}_3\text{Sb}_5\text{O}_{12}$ are the important ones.$^{[106]}$–$^{[108]}$ Following are the penta-antimonites obtained by hydrothermal technique:

$$\text{In}_3\text{Sb}_5\text{O}_{12}, \text{La}_3\text{Sb}_5\text{O}_{12}, \text{Pr}_3\text{Sb}_5\text{O}_{12}, \text{Tb}_3\text{Sb}_5\text{O}_{12}, \text{Yb}_3\text{Sb}_5\text{O}_{12}$$

The synthesis of these compounds is usually carried out by the hydrothermal technique within the temperature interval 450–550°C and $\Delta T = 0.5$ to 1.0°C, $P = 110–1100$ atm.

Variation in the ratio of $\text{R}_2\text{O}_3(\text{In}_2\text{O}_3)/\text{Sb}_2\text{O}_3$ in the nutrient limits the crystallization of the product with the appearance of $\text{Sb}_2\text{O}_3$ crystals. Higher concentration of KF or CsF results in formation of $\text{K}_3\text{RF}_6$ and both of these phases often reduce the output of penta-antimonites, field.

Penta-antimonite, $\text{In}_3\text{Sb}_5\text{O}_{12}$ forms in the aqueous solutions of KHF$_2$, KF (45–55wt%) and CsF (20 wt%). The crystals are 1–2 mm in size. The basic forms are hexagonal (1120) and trigonal (01T0) prisms, pyramids (01T2), (10T1), (0221) and (T32 T). This compound has three polymorphic modifications and two are reversible transformations: trigonal $\alpha$-form ($<140°C$), trigonal $\beta$-form (140–450°C) and cubic $\gamma$-form ($>450°C$).$^{[107]}$ Figure 9.25 shows the $\text{In}_3\text{Sb}_5\text{O}_{12}$ crystals obtained under hydrothermal conditions.$^{[108]}$ These crystals show interesting piezoelectric and ferroelectric properties.
Similarly, Sc$_3$Sb$_5$O$_{12}$ crystallizes in the aqueous solutions of KF with concentration up to 60 wt%. The synthesis of scandium pent-antimonite takes place simultaneously with the formation of K$_3$ScF$_6$ and attains 70% output in 30% KF solution; in aqueous solutions of CsF with concentrations of 12–60 wt% and Sc$_2$O$_3$/Sb$_2$O$_3$ ratio > 1:1, Sc$_3$Sb$_5$O$_{12}$ crystallizes with 100% output. The morphology of these crystals is similar to that of indium analogue.[108]

Rare earth antimonites with a general formula R$_3$Sb$_5$O$_{12}$ (R= La, Pr, Ti and Yb) are the important compounds in this group.[109] It is interesting to note that the lanthanum penta-antimonite crystallization field does not exist and its crystallization in aqueous solutions of KF with concentrations of 5–50 wt% is always accompanied by the related phases. Stefanovich et al. (1982) have studied the phase transformations in these rare earth antimonites in detail.[110] In the presence of an oxidizing agent, trivalent antimony oxidizes up to the pentavalent state forming antimonates and producing H[Sb(OH)$_6$]$_6$ acid. They are poorly soluble in water. There are several antimonate minerals and among the synthetic varieties, only a few compounds have been obtained: Na[SbO$_3$], Na$_3$Sb$_3$[Sb$_2$O$_{11}$] and Sb[SbO$_4$].[111][112] Figure 9.26 shows (a) the field of crystallization of antimonites in the system Na$_2$O-Sb$_2$O$_3$-Sb$_2$O$_5$-H$_2$O, and (b) field of synthesis of antimonites. Figure 9.27 shows the field of crystallization of antimony antimonates at (a) lower and (b) higher oxygen potential.[111] Synthesis is carried out in aqueous solutions in 70% NaOH, 60% KF and 13% KHF$_2$, at temperature 550°C, with 60–70% fill, and a temperature gradient of 20–35°C. In order to stabilize the pentavalent antimony,
10–15% H₂O₂ is added. In Sb₂O₃, the rich region (2.5:1) forms NaSbO₃; with the change in the oxygen potential in the system, other phases crystallizing in the system are Sb³⁺Sb⁵⁺O₄ and Na₃Sb₃⁺Sb₂⁵⁺O₁₁. In highly concentrated aqueous solution of NaOH (>42%), Na₃Sb₃⁺Sb₂⁵⁺O₁₁ crystals are formed into prisms up to 5 mm size. In this system, the field of crystallization of Sb³⁺Sb⁵⁺O₄ with 100% output doesn’t exist. Antimonates can be crystallized in the aqueous KF solutions with concentration 60% and 98% KHF₂ at temperatures of 450–550°C and 60–70% fill. In aqueous KHF₂ solutions, only two phases are formed: Sb₂O₃ and Sb³⁺Sb⁵⁺O₄. The antimony antimonates exhibit antiferroelectric properties.

Figure 9.26. (a) Field of crystallization of antimonates in the system Na₂O-Sb₂O₃-Sb₂O₅-H₂O and (b) field of synthesis of antimonites.

Figure 9.27. Field of crystallization of antimonates at (a) lower and (b) higher oxygen potentials.
9.7.3 Hydrothermal Synthesis of Garnets

Garnet, $Y_3Al_5O_{12}$, has extensively been used as a host lattice for luminescent ions and as substrates for the epitaxial deposition of magnetic garnets for magnetic bubbles. For these applications, large defect free crystals are requested. Though garnets are ordinarily grown from the flux, the hydrothermal technique is particularly suitable for the preparation of these mixed oxide crystals of high quality and large size. Such growth is easier to control on a seed and it takes place at a lower temperature than the flux growth.[113]–[115]

Yttrium aluminum garnet, $Y_3Al_5O_{12}$, crystallization has been studied in a variety of solvents including $(CO_3)^-$, $(OH)^-$ and halides. Among these, higher temperatures of synthesis are required for growth. Laudise and Kolb (1962); Kolb and Laudise (1975) have studied the phase equilibria of $Y_3Al_5O_{12}$ and $Y_3Fe_5O_{12}$ in the systems $Y_2O_3-Al_2O_3-H_2O$ and $Y_2O_3-Fe_2O_3-H_2O$ respectively.[116][117] Brochier et al. (1972) and Toudic and Passaret (1974) have studied the heteroepitaxial growth of thin $Y_3Fe_{5-x}Ga_xO_{12}$ and $Gd_yY_{3-y}Fe_{5-x}Ga_xO_{12}$ films under hydrothermal conditions using GdGaG as seed plates.[118][119] Similarly, there are several other reports on the hydrothermal epitaxial growth of garnet films.[120]–[123] Figure 9.28 shows the part of the phase diagram $Al_2O_3-Y_2O_3-H_2O$ between 350 and 450°C at a pressure of 25,000 psi, where the $K_2CO_3$ concentration is constant at 6M. $Gd_3Ga_5O_{12}$ appears to be incongruently saturating in contrast to $Y_3Al_5O_{12}$. Both growth rate and quality were poorer in $(CO_3)^-$ than in $(OH)^-$ at comparable concentrations. Indeed, in 6.0M $K_2CO_3$, under conditions where growth in $(OH)^-$ was appreciable, seeds grew a negligible amount or dissolved slightly. This is in contrast to $Al_2O_3$ (corundum) where $(CO_3)^-$, because of the higher coefficient of solubility, gives much larger rates than $(OH)^-$. Thus, $(CO_3)^-$ is preferable to $(OH)^-$. The optimum growth conditions for GdGa are:[117]

- **Excess Ga$_2$O$_3$**: 2.3M
- **Solvent**: 420°C
- **Growth temperature**: 80°C
- **Fill %**: 70–72%
- **Seed orientation**: (100) (111)
- **Growth rate**: as high as 0.6mm/day flawed; improved quality at rates near 0.25mm/day
These authors have obtained a wide range of garnets using flux grown nutrient:

- \( \text{Gd}_{2.34}\text{Tb}_{0.66}\text{Fe}_{12} \)
- \( \text{Eu}_{1.9}\text{Ga}_{1.1}\text{Al}_{0.3}\text{Fe}_{4.5}\text{O}_{12} \)
- \( \text{Er}_{2.0}\text{Eu}_{1.0}\text{Fe}_{4.5}\text{Ga}_{0.7}\text{O}_{12} \)
- \( \text{Er}_{1.0}\text{Eu}_{2.0}\text{Fe}_{4.3}\text{Ga}_{0.7}\text{O}_{12} \)
- \( \text{Ca}_{1.8}\text{Bi}_{1.2}\text{V}_{0.9}\text{Fe}_{4.1}\text{O}_{12} \)
- \( \text{Ca}_{2.0}\text{Bi}_{0.95}\text{V}_{0.95}\text{Fe}_{4.05}\text{O}_{12} \)

In most of the experiments on the hydrothermal growth of garnets, hydrothermal tipping is used to avoid the seed attack during the warm-up stage.

Figure 9.28. Phase diagram \( \text{Al}_{2}\text{O}_{3}-\text{Y}_{2}\text{O}_{3}-\text{H}_{2}\text{O} \) between 350 and 450°C.[117]
For the epitaxial film growth of $\text{Er}_{1.0}\text{Eu}_{2.0}\text{Fe}_{4.3}\text{Ga}_{0.7}\text{O}_{12}$ on (110) seeds of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, the following conditions have been employed by Laudise and Kolb (1975):\(^{[116]}\)

- Growth temperature: 330–445°C
- $\Delta T$: 40–80°
- Fill %: 60–65%
- Solvent: 10–20M KOH
- $\text{Ga}_2\text{O}_3$: 0.75M

Nijs et al. (1992) have obtained $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ under hydrothermal conditions at temperature 550°C and pressure 2 kb, and in the experimental duration of 14 days.\(^{[124]}\) Starting material was $\text{Al}_2\text{O}_3\cdot3\text{SiO}_2$ gel, into which ground metallic manganese was added to obtain a fine powder with composition $\text{Al}_2\text{O}_3\cdot3\text{SiO}_2\cdot3\text{Mn}$. This starting material, plus excess water, was taken in a gold capsule which was placed in a Tuttle vessel. After fourteen days, the capsule was opened to get small crystals of manganese garnet. This material shows red luminescence from the Mn$^{2+}$ ions, which is quenched at room temperature due to energy migration to quenching centers.

### 9.7.4 Hydrothermal Synthesis of Ferrite

Ferrites are important technological materials with great success in the development of magnetic oxide powders with a particle size in the nanometer range.\(^{[125]}\) Among them, barium hexaferrite and manganese ferrite are the most important ones. Both could be prepared through solid state sintering, chemical precipitation, melting, and hydrothermal methods.\(^{[126]}\)–\(^{[130]}\) Of these methods, the hydrothermal method is probably the most attractive one, because the resulting ferrite has a perfect crystal structure with a definite composition and very fine particle size (usually smaller than 1 µm) and is almost a monodispersed crystal. Therefore, the product obtained from hydrothermal synthesis can be used directly for ceramics processes without a calcination step.

Kumazawa et al. (1993) have synthesized barium ferrite fine particles from an aqueous suspension containing goethite and barium hydroxide by the hydrothermal method, and examined systematically the relation between the particle size and the reaction conditions commercially available, and also synthetic goethite particles are used in the
hydrothermal preparation of ferrites.\textsuperscript{[131]} The experimental temperature ranges from 200 to 300°C. Both with and without stirring techniques have been employed under hydrothermal conditions. Alpha-FeOOH is dehydrated to form $\alpha$-Fe$_2$O$_3$. The dehydration rate may increase with increasing outer surface area of the particle. The barium ferrite particle may be formed by the incorporation of barium ion under such conditions that $\alpha$-FeOH is dehydrated to form $\alpha$-Fe$_2$O$_3$. Similarly, barium hexaferrite particle is formed by dissolution followed by the crystallization. Usually the starting materials in the form of either hydroxides or nitrates of iron and barium, and mineralizer NaOH and water, are taken in the hydrothermal reactor and the slurry mixture is heated to a desired temperature. After the experimental run, the suspension is withdrawn from the reactor, neutralized by a diluted HCl solution and then filtered and washed thoroughly with water. The reaction can be written as follows:

$$12\text{FeOOH} + \text{Be(OH)}_2 \rightarrow \text{BaO} \cdot 6\text{Fe}_2\text{O}_3 + 7\text{H}_2\text{O}$$

Wang et al. (1991) have studied reaction mechanism of producing barium hexaferrites from $\alpha$-Fe$_2$O$_3$ and Ba(OH)$_2$ under hydrothermal conditions.\textsuperscript{[132]} Wang et al. (1993) have studied the kinetics of the crystallization of barium hexaferrite in detail.\textsuperscript{[133]} The reaction rate of producing barium hexaferrite was highly dependent on the concentrations of Fe(OH)$_4$ (aq), Ba(OH)$_2$ and NaOH in the aqueous solution. These authors have found that the reaction should be carried out at a temperature greater than 280°C to obtain the main desired product, BaO-6Fe$_2$O$_3$. A kinetic model, based on the homogenous phase reaction has been built to describe the dissolution of $\gamma$FeOOH (s) and the precipitation of the dissolved $\gamma$FeOOH (s) (or Fe(OH)$_4$ (aq)) and Ba(OH)$_2$ in sequence to produce the desired product, BaO-6Fe$_2$O$_3$. The reaction rate at 280°C is expressed as a function of Fe(OH)$_4$ (aq) and Ba$^{2+}$ concentration, i.e.

$$R_p = \frac{0.19[\text{Fe(OH)}_4]_{aq}[\text{Ba}^{2+}]}{1 + 8.6[\text{Fe(OH)}_4]_{aq}}$$

Figure 9.29 shows the effect of alkali concentration on the extent of conversion of the BaO-6Fe$_2$O$_3$: the reaction rate increases with the increase of the concentration of NaOH solution. Higher concentration of
NaOH also results in a higher yield of the production. The maximum yield of BaO·6Fe₂O₃ achieved is 81% for [OH⁻]=2N. In case of the nitrate source for the nutrient, the particle size decreased with an increase in alkali molar ratio defined as [OH⁻]/[NO₃⁻]. Particles about 0.1 µm in size were produced at molar ratios above six. As the concentration of NaOH increases, the mean size of the particles decreases. These experimental evidences may support the concept that during hydrothermal treatment at a constant temperature (e.g., 300°C), an increase in the crystallinity of precipitated particles mainly proceeds instead of particle growth driven by Ostwald ripening.

![Figure 9.29. Effect of alkali concentration on the conversion of the BaO·6Fe₂O₃.][133]

The synthesis of manganese ferrites is carried out in the same way as that of barium hexaferites. Wolski et al. (1995; 1997) have studied the hydrothermal synthesis and treatment of manganese ferrites in detail.[129],[130] The main problem associated with the manganese ferrites is the tendency of manganese to form an enormous number of individuals with various valencies, different O/Mn ratios, and with the vacancies
spread over different positions of the sublattices. Wolski et al. (1997) have studied the hydrothermal treatment of such phases to eliminate the non-magnetic traces from the product and also suggested the probable stages of conversion of $\text{Mn}_{0.5}\text{Fe}_{1.0}(\text{OH})_4$, for example, up to the product $\text{MnFe}_2\text{O}_4$, which is a ferri-magnetic spinel.$^{[130]}$

### 9.7.5 Hydrothermal Synthesis of Complex Oxides

The mixed/complex oxides represent only a small, but important and diversified part of the entire family of inorganic compounds. Mixed oxides are widely used as superionics, fillers, or pigments in pulp and paper, paint, and ceramic electronic industries, and so on. Most of these mixed or complex oxides have highly complex structures, and are highly heat-resistant and chemically inert. In the recent years, there has been a growing demand for these complex oxides, especially from the manganese family and other related transitional metal families owing to their unique layered structures.$^{[134]}$–$^{[136]}$ These advanced mixed oxides are those which present specific characteristics in their composition, such as pigments for electronics, or in their morphology, such as nanometer-size particles. The hydrothermal method is potentially superior for low cost production of advanced mixed oxides because complex oxide powders are formed directly. The temperature of synthesis lies between the boiling point of water and its critical temperature ($374^\circ\text{C}$), whereas the pressure can go as high as 15 MPa. The major advantages are the use of inexpensive raw materials such as oxides, hydroxides, chlorides and nitrates, control of growth rate, particle size, stoichiometry, particle shape, elimination of impurities, and so on.

Among these mixed oxides, manganese-bearing mixed oxides are very important as the majority of them show layered structures. Feng et al. (1996) have synthesized birnessite-type lithium manganese oxide, by reacting a $\text{Mn}(\text{NO}_3)_2$ solution with a mixed solution of $\text{H}_2\text{O}_2$ and $\text{LiOH}$ at room temperature.$^{[137]}$ This manganese oxide has a layered structure with a single sheet of crystal water and lithium ions between two-dimensional edge-shared $\text{MnO}_6$ octahedral sheets. The interlayer spaces can have $\text{Na}^+$, $\text{K}^+$, and $\text{Cs}^+$. Such manganese oxides can be used as metal ion adsorbents and cathodes for lithium rechargeable batteries.$^{[138]}$ $^{[139]}$ Figure 9.30 shows the structure of birnessite-type lithium manganese oxides. The lithium ions may locate between the $\text{MnO}_6$ octahedral sheets, and they can be topotactically exchanged with metal ions.
Manganese oxides like LiMn$_2$O$_4$ are of particular interest because they readily intercalate lithium into their structures and are therefore potentially useful as the cathode of lithium batteries. For example, SONY’s lithium ion cell uses the very expensive LiCoO$_2$ cathode. Hence, extensive research is currently underway to find promising candidates for cathode materials in lithium secondary batteries to replace the expensive cobalt used in present commercial cells. A manganese oxide that behaved like the layered LiCoO$_2$ would be a prime candidate for this application because of its high free energy of reaction with Li and relatively low cost.$^{[140]}$ The experiments involved reacting potassium permanganate with hydrochloric acid and then hydrothermally treating the reaction mixture. The overall reaction takes place as follows:

\[
\text{Eq. (13)} \quad \text{KMnO}_4 + \frac{(1 - x + 2y)}{2} \text{H}_2\text{O} \rightarrow \text{K}_2\text{MnO}_2 \cdot y\text{H}_2\text{O} \\
\quad + \frac{(1 - x)}{4} \text{KOH} + \frac{(3 + x)}{4} \text{O}_2
\]

Figure 9.31 shows the schematic diagram of layered manganates showing \(a\) anhydrous material, and \(b\) one water layer and two water layers.

Demazeau et al. (1994) have obtained La$_2$MnIrO$_6$ belonging to the perovskite family using a simple approach of ferromagnetic interactions through a 180°C super exchange. The structural and magnetic studies have confirmed the ferromagnetic behavior of such an oxide.$^{[135]}$ Turrillas et al. (1987) have synthesized Ca$_2$Pt$_3$O$_8$ under hydrothermal conditions.

![Figure 9.30. Structure of birnessite-type lithium manganese oxides.$^{[137]}$](image-url)
conditions ($T = 528^\circ C$, $P = 170$ MPa).\cite{141} The platinum ternary oxides have potential uses owing to their good ternary catalytic and electrochemical properties, and also semiconductor, insulator and metallic-conductor properties. Schwartz and Prewitt (1984) have studied the structure and properties of a large number of binary and ternary oxides of platinum.\cite{142} Usually KOH and water are used as mineralizers. These platinum compounds/oxides are insoluble in water, nitric acid, hydrochloric acid, or hot aqua-regia, but soluble in hot hydrobromic acid. The most prominent feature of Ca$_2$Pt$_3$O$_8$ is that it has three polymorphic modifications (tetragonal, orthorhombic and hexagonal).

![Figure 9.31. Schematic diagram of layered manganates showing (a) anhydrous material, (b) one water layer, and (c) two water layers.\cite{140}](image)
In recent years, there is a growing interest for stabilized yttria, ceria, and zirconia based catalysts, which also act as structural and electronic promoters of heterogeneous catalytic reactions and as oxide ion conducting solid electrolytes in electrochemical cells. A series of solid solutions based on the perovskite type structure showing the above mentioned physical and chemical properties are being hydrothermally prepared. The prominent members among them are:

\[
\begin{align*}
&\text{BaZr}_{1-x}\text{M}_x\text{O}_{3-x} \quad (M = \text{Al}, \text{Ga}, \text{In}; x = 0.20) \\
&\text{SrZr}_{0.3-\alpha} \quad (M = \text{Al}, \text{Ga}, \text{In}; x = 0.20) \\
&\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta} \\
&\text{Ce}_{1-x}\text{Bi}_x\text{O}_{2-\delta} \text{ and so on.} \quad [146]-[149]
\end{align*}
\]

The preparation of these solid solutions is carried out usually at temperatures of 150 to 250°C under autogeneous pressure. Morey type autoclaves, or other commercially available autoclaves like Parr, or Berghoff autoclaves provided with Teflon® liners are used for the synthesis of these oxides. The pH is maintained usually at higher levels (>10). The commonly used solvents are KOH or NH₄OH. Figure 9.32 shows the SEM photographs of BaZr₃ₓMₙO₉₃₋ₙ (M = Al, Ga, In; x = 0.20).

There are several other varieties of mixed oxides synthesized under hydrothermal conditions. Hydrothermal technique is especially suitable for obtaining such unique structures, which are impossible to obtain by other conventional methods.

Figure 9.32. SEM photographs of BaZr₃ₓMₙO₉₃₋ₙ (M = Al, Ga, In; x = 0.20). [146]
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10

Hydrothermal Processing of Materials

10.1 INTRODUCTION

The term *processing* is a broad term covering many branches of materials preparation, fabrication, or development. Hydrothermal processing of materials is used in a very broad sense in recent years, and in the 21st century, it will play a vital role in materials science and technology. Hydrothermal processing of materials encompasses processes like synthesis, crystal growth, treatment, fabrication, alteration, hot pressing, recycling, sintering, etc., under hydrothermal conditions. In this chapter, we shall discuss materials processing under hydrothermal conditions dealing with the preparation of ultrafine particles, ceramics, whiskers, composites, thin films, and reinforcement. As the demand for these materials increased, the hydrothermal technique gradually underwent a considerable amount of modification and adaptation. This chapter has been devoted to a rapid progress achieved in the hydrothermal technique to suit modern technological requirements. The technique is especially handy for the preparation of ceramics (PZT, alumina, zirconia, yttria, ceria, and several bioceramics), epitaxial growth of crystalline thin films, composites, and ultrafine particles with a desired shape.
10.2 HYDROTHERMAL PREPARATION OF ADVANCED CERAMICS

In the last twelve years, the science of ceramics has undergone a revolution almost as dramatic as the more familiar ones in electronics. Novel approaches in preparing and processing ceramic solids have been developed, ingenious ways of circumventing the age-old problem of brittleness have been introduced, and new markets have opened up in such areas as electronics, sensors, photonics, orthopaedics, catalysis mixed ionic and electronic conducting ceramics, advanced nitride ceramics, advanced cements, mineralizers, heat engines, functional ceramics related to energy conservation environmental issues and so on.[1][2]

Today’s advanced ceramics represent developments well beyond the imagination of even the few far-sighted scientists of twenty-five years ago who first perceived the remarkable potential of ceramic solids and established “ductile” engineering ceramics as a suitable objective for material researchers to pursue. Figure 10.1 shows the interactions of ceramics science with other technical fields.[1] Since 1980 much attention has been paid to hydrothermal processing of fine zirconia, ceria, and titania powders. Several methods were used to prepare fine zirconia, hafnia, titania, ceria, PZT particles (powders), under hydrothermal conditions.

Figure 10.1. Interactions of ceramics science with other technical fields.[1] (Courtesy of the National Academy Press, Washington, DC.)
Applications of hydrothermal reactions in ceramics include the following aspects: phase equilibria, ultrafine single crystals, ultrafine amorphous, single crystal growth, hydrothermal reaction sintering, hydrothermal sintering, hydrothermal crystallization, dissolving, corrosion, etching, composites (inorganic + organic, inorganic + inorganic), testing, thin films, radioactive waste management, hydrothermal oxidation, hydrothermal decomposition, hydrothermal anodic oxidation, RESA (reactive electrode submerged arc) process, etc. Table 10.1 provides comparison among the popularly adopted techniques of preparation of advanced oxide powder.[3]

Table 10.1. Advanced Oxide Powder Process Comparison (Somiya, S. 1989)

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>Sol-gel</th>
<th>Coprecipitation</th>
<th>Hydrothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>Low-moderate</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>State of development</td>
<td>Commercial</td>
<td>R &amp; D</td>
<td>Commercial/demonstration</td>
<td>Demonstration</td>
</tr>
<tr>
<td>Compositional control</td>
<td>Poor</td>
<td>Excellent</td>
<td>Good</td>
<td>Good-excellent</td>
</tr>
<tr>
<td>Morphology control</td>
<td>Poor</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>Powder reactivity</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>&lt; 99.5</td>
<td>&gt; 99.9</td>
<td>&gt; 99.5</td>
<td>&gt; 99.5</td>
</tr>
<tr>
<td>Calcination step</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Milling step</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>
The hydrothermal preparation of very fine powders is an excellent approach to ideal powders. The ideal powder should have the following parameters:

i. Fine powder less than 1µm
ii. Soft or no agglomeration
iii. Narrow particle size distribution
iv. Morphology sphere or equiaxed
v. Chemical composition controllable
vi. Microstructure controllable
vii. Uniformity
viii. Free flowing
ix. Less defects ..... Dense particle
x. Less stress
xi. Reactivity ..... Sinterability
xii. Crystallinity
xiii. Reproducibility
xiv. Process control

The shape of ceramic products obtained under hydrothermal conditions is highly varied and some common hydrothermal products are listed below:

i. Fine Powder (Single crystals or Amorphous)
ii. Fiber
iii. Hydrate ..... Cement
iv. Large single crystal
v. Sintered body
vi. Film

The major advantages of hydrothermal processing of ceramics are as follows:

i. High quality
ii. High purity
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iii. High rate of reaction
iv. Dispersion
v. Better shape control
vi. Pollution free
vii. Energy saving
viii. Low temperature operation
ix. Use of large volume of the equipment
x. New products
xi. Better nucleation control and so on

However, there are some disadvantages like equipment—autoclaves which are of complicated design, and the fact that it is expensive; cumbersome operations like assembling and dissembling; the fact that it is impossible to observe the actual process; solubility aspects; and problems related to surface chemistry. Table 10.2 lists some of the salient features of the ceramic synthesis by commonly used techniques.

10.2.1 Hydrothermal Preparation of Simple Oxide Ceramics

Zirconia ceramics are remarkable materials due to their excellent mechanical, electrical, thermal and optical properties.\[4]\[5] Physical and chemical properties associated with these characteristics are closely related to structures and phase changes. Therefore, numerous studies have been undertaken of phase diagrams and structural changes in the zirconia systems.\[6]\[8] There are many contradictions and discrepancies, especially around 1000°C. One of the most important steps in solving this problem is the study of metastable phase diagram.\[9]\[11] Yashima et al. (1996) have studied the problem of diffusionless cubic-tetragonal (c-t') phase transition, where t' emphasizes a metastable tetragonal phase.\[6]

Thus, it can be distinguished from the stable t, which is formed diffusionally. Figure 10.2 shows a metastable-stable phase diagram of the ZrO\(_2\) -CeO\(_2\) system that is depicted in a composition temperature field. On cooling from 1650°C, the high-temperature cubic phase (B) transforms without cationic diffusions into a metastable tetragonal phase below the tetragonal-cubic transformation. Such metastable phase boundary is drawn by dashed and dotted lines.\[12]
Table 10.2. Ceramics Synthesis (from the works of M. Yoshimura and S. Somiya)

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Composites</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol gel(hydrolysis of metal alkoxides), precipitation, coprecipitation</td>
<td>High product purity and homogeneity, crystal symmetry; metastable compounds with unique properties; narrow particle size distribution; lower sintering temperatures</td>
<td>May require calcination, sometimes milling; mixed alkoxides can cause inhomogeneity, non-stoichiometry; sometimes expensive raw materials</td>
<td>Oxides; LAS, mullite, spinel, cordierite</td>
<td>Down to 5 nm 0.1 to 5 µm</td>
</tr>
<tr>
<td>Evaporative decomposition solids</td>
<td>Wide range of chemical compositions; single-step process; no separate calcination or milling required</td>
<td>Hollow aggregates formed; precursor must decompose at low temperatures; excess carbon impurities may require calcination</td>
<td>Oxides, nonoxides, composites, fibers</td>
<td>1 to 20 µm</td>
</tr>
<tr>
<td>Hydrothermal processing</td>
<td>High surface area; 99% dense sintered powders; submicron particles with narrow size distribution; simple equipment; continuous; no milling or calcination; short reaction times; lower energy requirements</td>
<td>Requires moderate temperatures/pressures; requires additives (seed crystals), surface treatments</td>
<td>Y2O3-PSZ, Eu2O3-doped HfO2 lead-zirconate titanate, other oxides</td>
<td>Down to 8 nm</td>
</tr>
</tbody>
</table>

(Cont’d.)
Table 10.2 (Cont’d.)

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Composites</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid expansion of supercritical fluids</td>
<td>Wide range of compositions including amorphous powders and nonequilibrium materials; fast reaction times (10^-5 sec); lower temperatures than plasma process</td>
<td>Requires high pressures and temperature; corrosive solvents; some agglomeration; machined nozzles to improve morphology</td>
<td>Oxides; (SiO_2, GeO_2, SiO_2-GeO_2) fiber precursors (polycarbosilane); labile, explosive materials</td>
<td>0.01 to 1.3 µm (ceramics) &lt; 0.1 µm fiber, 1 µm particle (polymers)</td>
</tr>
<tr>
<td>Reductive dehalogenation of elemental halides</td>
<td>Low temperature, any combination of elemental halides that can be reduced by alkali metals</td>
<td>Crystallization requires higher temperatures; high speed high-shear stirring needed; starting materials can be expensive; reactions are explosive or combustible</td>
<td>Amorphous precursors of TiB_2, SiC, B_4C, and other borides and carbides, SiC/ TiC, SiC/TiN</td>
<td></td>
</tr>
</tbody>
</table>
Tani et al. (1982) have studied in detail the effect of mineralizers on the crystallization of solid solutions in the system ZrO$_2$-CeO$_2$ under hydrothermal conditions.\cite{13} Samples prepared by the coprecipitation method were treated under 100 MPa at 600°C for 2–72 hours using distilled water or a solution of alkaline metal (Li, Na, K) fluorides, chlorides, bromides, carbonates, nitrates, sulfates, or hydroxides, as mineralizers.

Somiya et al. (1990) have given the following flowchart for the hydrothermal homogeneous precipitation method, Fig. 10.3.\cite{14} The autoclaves used were: i) Tuttle type; ii) 500 cl; iii) 1000 ml; iv) 5000 ml; v) 20,000 ml, etc. The lining metals were Pt, Zr, and Ti.\cite{14} By this means, the authors could obtain very fine powders of ZrO$_2$ and Y$_2$O$_3$-ZrO$_2$ of size 20 nm, with a narrow size distribution, very high purity, excellent sinterability, less defects and controllable shapes. Hence, hydrothermal processing provides an excellent mean fraction by obtaining controlled shape and size from the ceramic particles.
In the hydrothermal oxidation of metals, pulverization and oxidation proceed simultaneously during the reaction with high-temperature, and high-purity water. These phenomena have been applied in the preparation of fine oxide powders (20 to 30 nm) of Fe₃O₄, Cr₂O₃, ZrO₂, HfO₂, Al₂O₃, and others at relatively lower temperatures (400 to 600°C). [15]–[19] Figures 10.4 (a–d) show the fine crystals of zirconia and ceria.[20] Figures 10.5 (a–c) show the representative photographs of hydrothermally processed ceramic powders.[20]

10.2.2 Hydrothermal Preparation of Perovskite Type of Mixed Oxide Ceramics

Alkaline earth titanates have always appeared in two types of stable phases: the pyrochlore and the perovskite structural. Between these, the high purity, fine perovskite titanates with exact stoichiometry are widely used as ferroelectric materials, owing to their excellent electric, pyroelectric, semiconducting and electro-optic properties. Hydrothermal processing is a very convenient technique for the preparation of various multicomponent oxide materials that have maximum utility in present day
electronics applications.[21]–[23] These multicomponent oxides from electronic ceramic or catalytic applications can be produced by hydrothermal synthesis at moderate temperatures and pressures (>100°C and 0.1 M Pa). The success of hydrothermal synthesis depends on the selection of precursors that are both reactive and cost effective as well as appropriate process condition variables, which include temperature, pH, and reagent concentration.[24] In the last decade, hundreds of publications have appeared in literature devoted to various aspects for preparation of these perovskite type oxides owing to their potential applications in modern technology. However, it is impossible to discuss every aspect of these perovskite types of oxides in this handbook which is devoted to all general aspects of hydrothermal technology.

The general formula for perovskite can be written as ABO₃, and for the solid solution A(BₓC₁₋ₓ)O₃, where 0 < x > 1, A = Ca, Sr, Ba, Pb, and Bi, B = Ti, and C = Zr.

![Figure 10.4.](image)

**Figure 10.4.** Fine crystals of zirconia and ceria. (*Photos by M. Yoshimura.*)
Figure 10.5. Representative photographs of hydrothermally processed ZrO$_2$ ceramic powders. (Photos courtesy of S. Somiya.)
Kutty and Balachandran (1984) have synthesized crystallization of perovskite \((x = 0.5)\) at 573 K starting with crystallization of PbO and mixed Zr-Ti gels, obtained by hydrolyzing TiOCl\(_2\) and ZrOCl\(_2\) and NH\(_3\) (aq). Beal (1987) obtained perovskite \((x = 0.5)\) at 573 K from mixtures of zirconia-titania gels, crystalline PbO, and various mineralizers. The author found that the purity and morphology of the product depended on the chemical identity of the mineralizers.

Dawson and Swartz (1992) have synthesized several solid solutions \((0 < x < 1)\) from the PZT family using aqueous gels obtained by hydrolyzing TiCl\(_4\) and ZrOCl\(_2\) in basic solutions. The slurry obtained, along with lead oxide and precursors of other elements (dopants), was hydrothermally treated at 573 K. It was found that the obtained solids had the same metal ion stoichiometry as the feeding material.

Riman and his group have done excellent work on the preparation of these PZT types of ceramics and have studied in detail the thermodynamics and kinetics of these systems. Also, they have developed a new approach—intelligent engineering—in order to transform hydrothermal synthesis from an empirically based technology to one that revolves around engineering principles. They approached this problem from a multidisciplinary perspective of chemistry, chemical engineering, and physical chemistry, which all embrace principles of thermodynamics and kinetics. Thermodynamic principles enable one to determine how to design a reaction to yield phase pure materials. Without this knowledge, it is impossible to distinguish a process that is being controlled by thermodynamics versus kinetics. These authors have studied all the possible reactions that may occur in the hydrothermal medium, more of a typical PZT system, for example, in the Ba-Ti and Pb-Ti systems. Following are the relevant equilibria in the Ba-Ti and Pb-Ti hydrothermal systems:

\[
\begin{align*}
\text{i. } & \quad \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \\
\text{ii. } & \quad \text{H}_2\text{O}_{(g)} = \text{H}_2\text{O} \\
\text{iii. } & \quad \text{TiO}_2_{(s)} = \text{OH}^- - \text{HTiO}_3^- \\
\text{iv. } & \quad \text{Ba(OH)}_2_{(s)} = \text{Ba}^{2+} + 2\text{OH}^- \\
\text{v. } & \quad \text{BaOH}^+ = \text{Ba}^{2+} + \text{OH}^- \\
\text{vi. } & \quad \text{BaTiO}_3_{(s)} + \text{H}_2\text{O} = \text{Ba}^{2+} + 2\text{OH}^- + \text{TiO}_2_{(s)} \\
\text{vii. } & \quad \text{Ba(OH)}_2\text{-8H}_2\text{O}_{(s)} = \text{Ba}^{2+} + 2\text{OH}^- + 8\text{H}_2\text{O} \\
\text{viii. } & \quad \text{BaO}_{(s)} + 2\text{H}^+ = \text{Ba}^{2+} + \text{H}_2\text{O} \\
\text{ix. } & \quad \text{Ba}_2\text{TiO}_4_{(s)} + 2\text{H}_2\text{O} = 2\text{Ba}^{2+} + 4\text{OH}^- + \text{TiO}_2_{(s)}
\end{align*}
\]
x. CO$_2$(g) = CO$_2$(aq)
xi. CO$_2$(aq) + H$_2$O = H$^+$ + HCO$_3^-$

xii. HCO$_3^-$ = H$^+$ + CO$_3^{2-}$

xiii. BaCO$_3$(s) = Ba$^{2+}$ + CO$_3^{2-}$
xiv. BaCO$_3$(aq) = Ba$^{2+}$ + CO$_3^{2-}$

xv. BaHCO$_3^+$ = Ba$^{2+}$ + HCO$_3^-$

xvi. Ti$_4^+$ + H$_2$O = TiOH$_3^+$ + H$^+$

xvii. TiOH$_3^+$ + H$_2$O = Ti(OH)$_2^{2+}$ + H$^+$

xviii. Ti(OH)$_2^{2+}$ + H$_2$O = Ti(OH)$_3^+$ + H$^+$

xix. Ti(OH)$_3^+$ + H$_2$O = Ti(OH)$_4^{4+}$ + H$^+$

xx. Ti(OH)$_4^{4+}$ + H$_2$O = Ti(OH)$_3^+$ + H$^+$

xxi. PbO (s) + H$_2$O = Pb$^{2+}$ + 2OH$^-$

xxii. PbO (aq) + H$_2$O = PbOH$^+$ + OH$^-$

xxiii. Pb(OH)$_2$ = Pb$^{2+}$ + 2OH$^-$

xxiv. Pb$^{2+}$ + 2OH$^-$ = H$^+$ + HPbO$_2^-$

xxv. Pb$^2+$ + H$_2$O = 2Pb$^{2+}$ + H$_2$O

xxvi. Pb$^{2+}$ + H$_2$O = 3Pb$^{2+}$ + 4OH$^-$

xxvii. Pb$^{2+}$ + 2OH$^-$ = H$^+$ + HPbO$_2^-$

xxviii. Pb$^{2+}$ + 2OH$^-$ = 4Pb$^{2+}$ + 4OH$^-$

xxix. Pb$^{2+}$ + 2OH$^-$ = 6Pb$^{2+}$ + 8OH$^-$

xxx. PbTiO$_3$(s) + H$_2$O = Pb$^{2+}$ + 2OH$^-$ + TiO$_2$(s)

About thirty independent reactions consisting of thirty-one species are shown above.

Aksay et al. (1996) have prepared nanometer sized BaTiO$_3$ particles under hydrothermal conditions by dispersing TiO$_2$ powders in a concentrated aqueous solution of Ba(OH)$_2$.[33] The TiO$_2$ particles dissolve in the aqueous Ba(OH)$_2$ solution and lead to the nucleation of nanometer-sized cubic phase BaTiO$_3$ particles. In concentrated solutions, the BaTiO$_3$ particles grow through multiple clustering. These authors have used a similar approach to obtain BaTiO$_3$ films from organo-metallic precursors at 80°C and below. It was found that the grain size of the film depends on the nucleation rate of the BaTiO$_3$ particles.
For the preparation of fine particles of this perovskite type mixed oxide, knowledge of stability diagrams under hydrothermal conditions is very important. The stability diagram shows the regions of reagent concentrations and pH at which various species predominate in the system, Fig. 10.6. Thus, the stability diagrams indicate the optimum synthesis conditions for which desirable products are thermodynamically stable. However, the stability diagrams were considered for a limited number of hydrothermal systems on the assumption that the aqueous solutions were ideal.[34][35] They are especially inaccurate when concentrated electrolyte solutions are utilized or when a multitude of competing reactions occur in a solution, thus making the equilibrium concentrations of various species strongly dependent on activity coefficients. Similarly, the speciation diagrams and yield diagrams help greatly in the hydrothermal synthesis of phase-pure ceramics. Figure 10.7 shows the calculated yield of PbTiO3 in the Pb-Ti-H2O complexing agent system for various Pb/Ti ratios. A majority of the PZT systems incorporate intolerable amounts of alkaline metals, which are introduced in the form of mineralizers. In recent years, organic mineralizers are being used by a large number of workers. For example, Riman (1996) has found that tetramethylammonium hydroxide [N(CH3)4OH] is a favorable substitute for alkaline metal hydroxide mineralizers in producing phase-pure PZT.[31] Phase-pure MeTiO3 (Me = Ca, Sr, Ba) can be obtained at input molalities of Ba, Sr, and Ca greater than 7 × 10⁻⁵, 10⁻⁶ and 5 × 10⁻⁵, respectively. Otherwise, the relative location of the 99.995% yield regions for the three titanates will be similar to the pattern noted for stability diagrams. In concentrated solutions, the consumption of OH⁻ ions is caused by the following predominant reactions:

\[ \text{Eq. (1)} \quad \text{Me}^{2+} + \text{TiO}_2 + 2\text{OH}^- = \text{MeTiO}_3 + \text{H}_2\text{O} \]

Thus, 2 molar of OH⁻ is consumed for the synthesis of 1 molar of MeTiO₃, and only a relatively small amount of OH⁻ is necessary to ensure correct pH for respective alkaline earth. Unlike the synthesis with nitrates, the use of metal hydroxide precursors at high concentrations does not require the addition of a mineralizer because the necessary concentration of OH⁻ groups is readily provided by the hydroxide precursor. To the contrary, at dilute concentrations identical amounts of mineralizers are needed, irrespective of whether a nitrate or a hydroxide is used as precursor. However, the required mineralizer concentration differs substantially for the three
metals. This may be caused by the strong, specific effects of the chemical identity of cations on activity coefficients due to their high concentration to form alkaline-earth titanates.

Figure 10.6. Stability diagram for barium titanate system.\textsuperscript{[31]}

Figure 10.7. Calculated yield of PbTiO\textsubscript{3} in the Pb-Ti-H\textsubscript{2}O complexing agent system for various Pb/Ti ratios.\textsuperscript{[31]}
Eckert, Jr. et al. (1996) have proposed *in situ* reaction mechanism, and dissolution-precipitation reaction mechanism, Figs. 10.8 and 10.9.[30] As evident from these figures, the *in situ* transformation model assumes that TiO₂ reacts initially with dissolved barium. This produces a continuous layer of BaTiO₃ through which additional barium must diffuse in order to continue reaction until the TiO₂ supply is exhausted. The product layer may be either a dense or a porous layer or of monocrystalline or polycrystalline nature. The dissolution-precipitation model involves multiple steps. For an anhydrous TiO₂ precursor, Ti-O bonds must be broken via hydrolytic attack, to form hydroxy-titanium complexes (Ti(OH)₄-x) capable of dissolution and reaction with barium ions or complexes (Ba²⁺ or BaOH⁺) in solution to precipitate BaTiO₃. In contrast, use of a hydrous TiO₂ reactant bypasses some, or most of the hydroxylation steps. BaTiO₃ nuclei may either originate at the TiO₂ substrate (heterogeneous nucleation) or form directly in the bulk solution (homogeneous nucleation). When heterogeneous nucleation occurs, the dissolving TiO₂ particle can be encapsulated, thereby limiting the supply of soluble TiO₂ species available to react with the barium species. As with the *in situ* transformation model, this diffusional barrier serves to slow if not to halt the hydrothermal reaction. Such mechanisms of formation of BaTiO₃ can also be applied to other perovskite type titanates. Figure 10.10 shows the perovskite type alkaline-earth titanates prepared under hydrothermal conditions.[23][33] The pH of the medium, precursor and the ratio of Me/Ti play an important role in determining the morphology of these particles.

![Diagram](Image)

*Figure 10.8. In situ reaction mechanism.*[30]
Figure 10.9. Dissolution-precipitation reaction mechanism.\cite{30}

Figure 10.10. Perovskite type alkaline-earth titanates. (a) See Ref. 23 and (b) see Ref. 33.
The preparation of alkaline-earth titanates has been carried out using non-aqueous solutions, which come under solvothermal synthesis. This has some advantage, as the solvothermal synthesis might allow the product to be free from foreign atoms because the organic solution, having a low relative permittivity, is free of ionic species. Chen and Xu (1998) have synthesized PbTiO$_3$ powder under solvothermal conditions.\textsuperscript{[36]} The starting materials involved are amorphous xerogels consisting of a mixture of equivalent molar amounts of PbO and TiO$_2$ (1:1 ratio), prepared by using lead acetylacate and tetrabutyl titanate. The precursor xerogel was poured into the solvent to form a suspension solution and 30.0 cm$^3$ of the suspension was fed into a 40 ml capacity stainless steel autoclave with a teflon liner. The required amount of methanol was poured into the autoclave and the autoclave was held at 240°C for 10 to 60 hours. The crystallinity increased with the increasing reaction time.

Although the crystallization of PbTiO$_3$ in alcohol solution required higher temperatures for longer times, the nanometer-sized particles, in comparison with the micrometer-sized ones derived from aqueous solution, exhibited a lower agglomeration due to the organic materials having a lower relative permittivity and a simple mode of size distribution.

Like the hydrothermal process, the formation of PbTiO$_3$ proceeds in alcohol solution by a dissolution-reprecipitation mechanism, in which the dissolution of precursor is the rate controlling stage. In comparison with those in methanol, the reactions in MOE for the syntheses of PbTiO$_3$ powders required higher temperatures or longer time because of MOE having a lower vaporizing pressure and relative permittivity.

Kaiser et al. (1994) have synthesized BaTiO$_3$ powders at a temperature of 175°C and pressures between 0.1 MPa and 1 MPa, starting from TiO$_2$.xH$_2$O and Ba(OH)$_2$.8H$_2$O in solvents of pure water, 1.5–pentanediol and in different mixtures of both using the lyothermal method.\textsuperscript{[37]} Figure 10.11 shows the schematic preparation route for lyothermal synthesis of BaTiO$_3$.

The authors could control the size and habit of BaTiO3 particles through the viscosity of the solvent and the concentration of the starting materials. The lyothermal method offers a promising means of producing various nanocrystalline materials of alkaline-earth titanates. Table 10.3 lists fine powders synthesized under hydrothermal conditions.
Figure 10.11. Schematic preparation route for lyothermal synthesis of BaTiO₃.\(^{[37]}\)

Table 10.3. List of Fine Powders Synthesized Under Hydrothermal Conditions (Courtesy of Prof. S. Somiya)

<table>
<thead>
<tr>
<th>Powder Type</th>
<th>Formula/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlO-OH</td>
<td>ZrO₂, Al₂O₃, ZrO₂-H₂O₂</td>
</tr>
<tr>
<td>FeO-OH</td>
<td>ZrO₂, SiO₂-ZrO₂</td>
</tr>
<tr>
<td>Cr₂O₃-H₂O</td>
<td>SiO₂-ZrO₂</td>
</tr>
<tr>
<td>MnO₃H₄O</td>
<td>Mn₂O₅, Nb₂O₅, ZrO₂-TiO₂</td>
</tr>
<tr>
<td>MnO₂H₂O</td>
<td>UO₂, TiO₂, Al₂O₃-H₂O₂</td>
</tr>
<tr>
<td>Mn₃O₄H₄O</td>
<td>Al₂O₃, Fe₂O₄</td>
</tr>
<tr>
<td>FeO</td>
<td>ZnO, NiO-Fe₂O₄, KMF₃</td>
</tr>
<tr>
<td>Cu₂O, ZnO</td>
<td>CoO, Y₂O₃-ZrO₂, Al₂O₃-ZrO₂, NdP₂O₅</td>
</tr>
<tr>
<td>NiO, MgO</td>
<td>CoO-ZrO₂, Al₂O₃-ZrO₂</td>
</tr>
<tr>
<td>CdO, CeO₂</td>
<td>V₂O₅, MgO-ZrO₂, Ta₂O₅, NdP₂O₅, Sm</td>
</tr>
<tr>
<td>PbO₂</td>
<td>TiO₂, Sr₂LaF₃, YAG</td>
</tr>
<tr>
<td>TiOSO₄·xH₂SO₄·xH₂O</td>
<td>TiO₂·xH₂O</td>
</tr>
<tr>
<td>Ba(OH)₂·8H₂O</td>
<td>Treatment in a pressure vessel, BaTiO₃</td>
</tr>
<tr>
<td>dissolution in H₂O</td>
<td>adding of NH₃(pH&gt;7)</td>
</tr>
<tr>
<td>washing with H₂O solvent:</td>
<td>water / 1.5 - pentanediol</td>
</tr>
<tr>
<td>reaction time = 1-120 hour</td>
<td></td>
</tr>
</tbody>
</table>

Table 10.3. List of Fine Powders Synthesized Under Hydrothermal Conditions (Courtesy of Prof. S. Somiya)

<table>
<thead>
<tr>
<th>Powder Type</th>
<th>Formula/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-Ferrites</td>
<td>NiFe₂O₄, Niobates, PbZr₂Ti₁₋ₓOₓ (0.46 &lt; x &lt; 0.75)</td>
</tr>
<tr>
<td>Sr-Ferrite</td>
<td>ZnFe₂O₄, Tantalates, Co₁₀ (PO₄)₆ (OH)₂</td>
</tr>
<tr>
<td></td>
<td>Ni₅Zn₅Fe₂O₄, Faradates, Ba Titanate</td>
</tr>
<tr>
<td></td>
<td>CoFe₂O₄, Titanate, Pb Titanate</td>
</tr>
<tr>
<td></td>
<td>Mn₀.₅Zn₀.₅Fe₂O₄, Rb₂(MoO₃)₃SeO₃, Tiₓ(MoO₃)₂SeO₃</td>
</tr>
<tr>
<td></td>
<td>Na Beidellite</td>
</tr>
</tbody>
</table>
In recent years, glycothermal and solvothermal syntheses are being used popularly to prepare fine powders of nitrides, alumina, iron oxide, hexaferrites, and so on. These methods are very useful in obtaining shaped and sized particles under relatively lower pressure temperature conditions.

10.2.3 Hydrothermal Processing of Bioceramics

Bioceramics represent a broad spectrum of ceramic materials designed for chemical compatibility and optimal mechanical strength with the physiological environment. These materials are used for the repair and reconstruction of diseased or damaged parts of the musculo-skeletal system. Bioceramics may be bioinert (alumina, zirconia), resorbable (tricalcium phosphate), bio-active (hydroxyapatite), bio-active glasses, and glass ceramics, or porous for tissue in-growth (HAp coated metals, alumina). Applications include replacements for hips, knees, teeth, tendons, and ligaments and repair of periodontal disease, maxillofacial reconstruction, augment and stabilization of the jaw bone, spinal fusion, and bone fillers after tumor surgery. Table 10.4 gives the types of bioceramics and also the tissue attachment and bioceramic classification. Bioceramics are also widely used in dentistry as restorative materials, gold porcelain crowns, glass-filled ionomer cements, dentures, etc.

High-density, high-purity (>99.5%) Al₂O₃ (α-alumina) was the first bioceramic, widely used for clinical purposes during the 1960s. It is used in total hip prostheses and dental implants because of its combination of excellent corrosion resistance, good bio-compatibility, low friction, high wear resistance, and high strength. Other clinical applications of Al₂O₃ include knee prostheses, bone screws, alveolar ridge (jaw bone), and maxillofacial reconstructs, ossicular (middle ear) bone substitutes, Keratoprosthesis (Corneal replacements), segmental bone replacements, blade and screw and post-type dental implants.

Zirconia (ZrO₂), in tetragonal form, stabilized by either magnesium or yttrium, has also been developed as a medical-grade bioceramic for use in total joint prostheses. The interest in ZrO₂ is derived from its high fracture toughness and tensile strength. These improved properties make it possible to manufacture femoral heads for total hip prostheses that are smaller than the present generation of Al₂O₃ heads. ZrO₂ implants are now used clinically; however, only implant survivability data over a ten year period will establish clinical advantages.
Table 10.4. Types of Bioceramic Tissue Attachment and Bioceramic Classification\cite{44}

<table>
<thead>
<tr>
<th>Type of Attachment</th>
<th>Type of Bioceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense, nonporous, almost inert ceramics attach by bone growth by cementing the device into the tissue, or by press-fitting into a defect (morphological fixation)</td>
<td>Al₂O₃, ZrO₂</td>
</tr>
<tr>
<td>For porous implants, bone ingrowth occurs, which mechanically attaches the bone to the material (biological fixation)</td>
<td>Porous hydroxyapatite, Hydroxyapatite-coated porous metals</td>
</tr>
<tr>
<td>Surface-reactive ceramics, glasses, and glass-ceramics attach directly by chemical bonding with the bone (bioactive fixation)</td>
<td>Bioactive glasses, Bioactive glass-ceramics, Dense hydroxyapatite</td>
</tr>
<tr>
<td>Resorbable ceramics and glasses in bulk or powder form designed to be slowly replaced by bone</td>
<td>Calcium sulfate (plaster of Paris), Tricalcium phosphate, Calcium phosphate salts, Bioactive glasses</td>
</tr>
</tbody>
</table>

These materials are prepared by hydrothermal techniques such as hydrothermal sintering, hydrothermal hot pressing and under hot isostatic pressure.

The most significant area of growth for bioceramics, however, involves a more complex material—hydroxyapatite \( \text{Ca}_{10} \left( \text{PO}_4 \right)_6 \left( \text{OH} \right)_2 \), which is the main mineral constituent of teeth and bones, representing 69% by weight. Hydroxyapatite based bioceramics have been in use in medicine and dentistry for twenty years.\cite{46}-\cite{49} It has the physicochemical advantages of stability, inertness, and biocompatibility. However, its relatively low strength and toughness, produced little interest among researchers searching for bulk structural materials. HAp ceramics do not exhibit any cytotoxic effects, and HAp can directly bond to the bone. Unfortunately, due to low reliability, especially in wet environments, the HAp ceramics can not be used for heavy load-bearing applications, like
Hydrothermal Processing of Materials

 Nevertheless, there has been a lot of research aiming to fabricate more mechanically reliable bioactive ceramics including, of course, the HAp materials. Suchanek and Yoshimura (1998) have reviewed in detail the past, present, and future of the HAp-based biomaterials from the point of view of preparation of hard tissue replacement implants.[50] The chemical component of the mineral constituents of teeth and bones is very important in the synthesis of HAp-based biomaterials. The inorganic phases present in the hard tissues contain mostly Ca$^{2+}$ and P, considerable amounts of Na$^+$, Mg$^{2+}$, K$^+$, also CO$_3^{-}$, F$, $ Cl$^-$ and H$_2$O. All these species, if applied in appropriate quantities, should be well tolerated in the implant by the surrounding tissues.

 Presently, the HAp-bioceramics are at the pinnacle stage of their development. Powder processing, formation, and densification have been understood quite well, allowing the control of chemical composition and microstructures of both dense and porous HAp ceramics. Any new developments concerning powder preparation/shaping/densification may affect only the price of the products, but are not expected to affect their medical applications, which are restricted due to the nature of HAp.[50]

 Several techniques have been used for the preparation of HAp powders.[51]–[54] Two main ways for the preparation of HAp powders are wet methods and solid state reactions. In the case of HAp fabrication, the wet methods can be divided into three groups: precipitation, hydrothermal technique, and hydrolysis of other calcium phosphates. Depending upon the technique, materials with various morphology, stoichiometry, and level of crystallinity, can be obtained. Solid state reactions usually give a stoichiometric and well-crystallized product, but they require relatively high temperatures and long heat-treatment times. Moreover, the sinterability of such powders is usually low. In the case of precipitation, nanometer size crystals can be prepared, and they have the shapes of blades, needles, rods, or equiaxed particles. Their crystallinity and Ca/P ratio depend mainly upon the preparation conditions and are in many cases lower than for well-crystallized stoichiometric hydroxyapatite. The hydrothermal technique usually gives HAp materials with a high degree of crystallinity and with a Ca/P ratio close to the stoichiometric value. Their crystal size is in the range of nanometers to millimeters. Hydrolysis of tricalcium phosphate, monetite, brushite, or octacalcium phosphate, requires low temperatures (usually below 100°C) and results in HAp needles or blades the size of microns. There are also alternative methods of HAp powders preparation, like sol-gel, flux method, electrocrystallization,
spray-pyrolysis, freeze-drying, microwave irradiation, mechano-chemical method, or emulsion processing.\[55\]–\[60\]

Many HAp powders can be sintered up to theoretical density, without pressure, at moderate temperatures (1000–1200°C). Processing at higher temperatures may lead to exaggerated grain growth and decomposition of HAp and, subsequently, to strength degradation HP, HIP, or HIP—post-sintering makes it possible to decrease the temperature of the densification process, decrease the grain size, and achieve higher densities. This leads to finer microstructures, higher thermal stability of HAp, and subsequently, better mechanical properties of the prepared HAp ceramics.\[50\] HAp ceramics, in a porous form, have been widely applied as bone substitutes. Porous HAp exhibits strong bonding to bone. The classical way to fabricate porous HAp ceramics (pore size of 100–600 µm) is through hydrothermal sintering of the HAp powder with appropriate pore-creating additives, like naphthalene, paraffin, hydrogen peroxide, etc., which evolve gases at elevated temperatures. Natural porous materials, like coral skeletons made of CaCO\textsubscript{3}, can be converted into HAp under hydrothermal conditions (250°C, 24–48 h).\[61\] Microstructure, undamaged porous HAp structures can also be obtained by HHP.\[62\] This technique allows solidification of HAp powder at 100–300°C, 30 MPa, for 2 hours.

Calcium phosphate bone cements find extensive applications as important biomaterials. These are mixtures of various calcium phosphate powders, such as CaHPO\textsubscript{4}·2H\textsubscript{2}O, Ca\textsubscript{4}(PO\textsubscript{4})\textsubscript{2}O, CaHPO\textsubscript{4}, Ca\textsubscript{8}H\textsubscript{2}(PO\textsubscript{4})\textsubscript{6}·5H\textsubscript{2}O, Ca(H\textsubscript{2}PO\textsubscript{4})\textsubscript{2}H\textsubscript{2}O, or TCP and water, or another liquid (for example, H\textsubscript{3}PO\textsubscript{4} or Na\textsubscript{2}HPO\textsubscript{4}). The mixture transforms into HAp during setting, forming a porous body, even at 37°C.\[64\]–\[66\] The setting time of calcium phosphate cements can be reduced to a few minutes. Similarly, the decay of cements, when in contact with blood, can be prevented. Several types of cements like HAp clays, consisting of HAp granules in a saline solution of calcium alginate, bioactive glass bone cements, HAp-, TCP-, or bioactive glass-reinforced polymeric bone cements, have also been developed.

The advantages of the calcium phosphate bone cements are high biocompatibility, bioactivity, and osteoconductivity. The only serious disadvantage is their relatively poor mechanical strength. Easy shaping of bone cements enables using them to fill bone defects much better than HAp solid blocks, which are difficult to shape, or HAp powders/granules, which are difficult to keep in place. Calcium phosphate bone cements
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may, in the future, replace PMMA cements as bone/implant fixation, if their mechanical properties can be improved. Moreover, they can be used as fillings of tooth root canals or as drug-delivery systems. The hydrothermal method has several advantages in treating these calcium phosphate bone cements and slurries in a simple and effective way.

The future of HAp-based bioceramics lies in HAp-based composites, like HAp-ceramic, HAp-metal, HAp-polymer, HAp-collagen, and so on. However, there remain several unanswered questions related to HAp bioceramics: such as, is it possible to make HAp-based ceramics applicable to heavy-loaded implants? Hydrothermal processing plays a key role in the preparation of bioceramics. A combination of methods, like sol-gel and hydrothermal processing, also help greatly in the development or processing of future bioceramics.

10.2.4 Hydrothermal Preparation of Thin Films

This is one of the fast developing areas in hydrothermal research. The epitaxial growth of thin films under hydrothermal conditions began during the 1970s. The heteroepitaxial growth of single crystal films of YIG on GGG substrates by hydrothermal synthesis has been reported by many workers. In present day context, the method has been modified and is popularly known as the hydrothermal-electrochemical technique, which is a very convenient method of preparing a wide range of films on substrates, coating of materials, preparation of multi-layered compounds, functionally gradient materials, and so on. The method is especially versatile and convenient, because of the lower temperature and pressure conditions involved compared to the conventional hydrothermal technique involving very high-pressure–temperature conditions. Among the compounds obtained through hydrothermal-electrochemical technique, perovskite type alkaline-earth titanates dominate, followed by tungstates, molybdates, and a series of solid solutions of alkaline earth titanates.

Synthesis of large PbTiO₃ single crystals and polycrystallized ceramics is very difficult because it cracks spontaneously when passing through its phase transformation temperature ($T_c = 490°C$) during cooling. Possible applications in electronic and optical devices have brought much attention to the preparation of pure PbTiO₃ film. Most of the films have been fabricated by either rf sputtering or chemical vapor deposition. However, these methods have several disadvantages, such
as the stoichiometric change of the film composition and residue of source material, such as PbCl₂, in the film. Furthermore, to form ferroelectric PbTiO₃ films during or after processing, requires high-temperature treatment, which causes a reaction of the film with the substrate and sometimes leads to cracking and/or peeling of the film. Metal-organic chemical vapor deposition (MOCVD) and sol-gel methods have also been applied to the preparation of PbTiO₃ film.[77]–[81]

During processing, high temperatures above 500°C are also needed to remove organics. On the other hand, hydrothermal synthesis has frequently been used in preparing ceramic powders for a variety of applications. It is superior to the other powder preparation methods since high-temperature calcination is not necessary for the synthesis of crystallized ceramic powder. Verification can be supported by the experimental results of hydrothermal synthesis of PbTiO₃ powders.

During the 1990s, several authors developed hydrothermal or hydrothermal-electrochemical methods to prepare various double oxides such as BaTiO₃ and SrTiO₃ crystallized films directly on Ti-metal substrates by taking advantage of the hydrothermal reactions in high-temperature water (200°C).[82]–[90] This method, in general, enables us to synthesize perovskite-type compound ABO₃, on a B-site metal in an aqueous alkaline solution containing A-site elements. It is increasingly being used for the preparations of BaTiO₃ film by other groups as well.

In the hydrothermal-electrochemical method, BaTiO₃ films are produced on a titanium electrode, which is anodized in the presence of an electrolyte containing Ba(OH)₂ under pressurized conditions. Recent results indicate that polycrystalline BaTiO₃ films can be prepared at temperatures as low as 55°C, using electrochemical activation in a barium acetate electrolyte in an oxygen atmosphere.[91] This method has been used as a highly versatile one to prepare perovskite films of several materials such as BaTiO₃ and SrTiO₃,[83]–[85] CaTiO₃,[87] BaFeO₃,[85] LiNbO₃,[85] BaNbO₃,[87] Ba₂Nb₃O₁₀,[87] PbTiO₃,[76] BaWO₄,[74] TiO₂,[93] ZnO,[94] and TiO₃,[95] etc.

A closely related technique for film formation is hydrothermal deposition in which perovskite films are produced under similar conditions, but without electrochemical activation. By this technique, BaTiO₃,[3][96] SrTiO₃,[83] (Ba, Sr) TiO₃ and BaZrO₃,[96][97] films have been obtained.

The hydrothermal-electrochemical film formation technique is not yet well established and there is not much information on the
electrochemical mechanism involved in the formation of these films. Moreover, there is not a clear understanding of the relationship between the film formation mechanisms for the hydrothermal method and those for the hydrothermal-electrochemical method. Most of the earlier works on BaTiO$_3$ hydrothermal-electrochemical formation has been performed in two-electrode cells, titanium anode and platinum cathode. In such a system, it is not possible to obtain accurate, specific, information on the electrochemical phenomena occurring at the titanium anode as the measured voltage drop on the cell is the result of processes at the anode, cathode, and in the electrolyte.

Kajiyoshi et al. (1995) have described the autoclave designed for hydrothermal-electrochemical treatment/preparation of ATiO$_3$ (A = Ba, Sr) thin films. It has a 3-electrode technique. The electrolytic cell assembled in the autoclave is shown schematically in Fig. 10.12. It accommodates an Ag/AgCl external reference electrode (Toshin Kogyo, Tokyo, Japan), which enables one to measure potentials of electrodes on a thermodynamically meaningful scale, regardless of the electrolysis conditions. The preprocessed Ti substrate and the platinum plate are suspended as the working electrode (anode) and the counter electrode (cathode), respectively, by 0.5 mm diameter wires of the same metal as the respective plates, keeping an interval of 30 mm between them in the electrolytic cell containing 500 ml of the solution. The experiments were carried out at 150°C, an approximate heating rate being 1.5°C/min. The Ti working electrode was polarized potentiostatically from 50°C in the heating region to the end of the 150°C isothermal region, keeping an anodic potential of +12.0 V vs. Ag/AgCl. The electrolysis current varies characteristically in the heating process and then remains almost constant in the isothermal process. After the experiment, the Ti substrate was washed in distilled water with an ultrasonic cleaner and dried at 120°C. Kajiyoshi et al. (1995) have also studied, in detail, the transport mechanism of film-constituting elements. They propose two models; the first based on the principle of tracer technique: i) substitutional transport, ii) interstitial transport. The second is the short-circuit path model. The latter one is more appropriate here to describe the mass transport in ATiO$_3$ (A = Ba, Sr). Figure 10.13 illustrates schematically the mass transport and film growth mechanisms of the short-circuit path model. In this model, all the observed results can be explained comprehensively, together with an atom-mixing mechanism accompanied by the dissolution-recrystallization