HYDROTHERMAL PROCESSING

1. Introduction

Hydrothermal processing of advanced materials has becoming popular among scientists and technologists of different disciplines, for the last 20 years. The term Hydrothermal is purely of geological origin. It was first used by the British Geologist, Sir Roderick Murchison (1792–1871), to describe the action of water at elevated temperature and pressure, in bringing about changes in the earth's crust leading to the formation of various rocks and minerals (1). It is well known that the largest single crystal formed in Nature (beryl crystal of >1000 g) and some of the largest quantities of single crystals created by humans in one experimental run (quartz crystals of several thousands of gram) are both of hydrothermal origin.

The term advanced material refers to a chemical substance, whether organic or inorganic in composition possessing the desired physical and chemical properties. In current context, the term materials processing is used in a very broad sense to cover all sets of technologies and processes of materials preparation to meet the demand from a wide range of industrial sectors. Obviously, it refers to the preparation of materials with a desired application potential. Among various technologies available today in advanced materials processing, the hydrothermal technique occupies a unique place owing to its advantages over conventional technologies. It covers processes like hydrothermal synthesis, hydrothermal crystal growth leading to the preparation of fine-to-ultrafine crystals, bulk single crystals, hydrothermal alteration, hydrothermal sintering, hydrothermal decomposition, hydrothermal stabilization of structures, hydrothermal dehydration, hydrothermal extraction, hydrothermal treatment, hydrothermal phase equilibria, hydrothermal electrochemical reaction, hydrothermal recycling, hydrothermal microwave, hydrothermal-mechanochemical, hydrothermal fabrication, hot pressing, hydrothermal metal reduction, hydrothermal leaching, hydrothermal corrosion, etc. The hydrothermal processing of advanced materials has many advantages, such as high product purity and homogeneity, crystal symmetry, metastable compounds with unique properties, narrow particle size distribution, lower sintering temperature, a wide range of chemical compositions, single-step process, dense sintered powders, submicron particles with narrow size distribution, simple equipment, lower energy requirements, fast reaction times, growth of crystals with polymorphic modifications, growth of crystals with very low solubility, and a host of others.

Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Byrappa and Yoshimura (2001) define *hydrothermal* as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at a pressure >1 atm in a closed system (1). However, there is still some confusion with regard to the very usage of the term hydrothermal. For example, chemists prefer to use a term, viz, *solvothermal*, meaning any chemical reaction in the presence of a non-aqueous solvent or solvent in supercritical or near supercritical

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conditions. Similarly, there are several other terms like *glycothermal, alcothermal, ammonothermal*, etc. Here, the term hydrothermal is used throughout the text to describe all the heterogeneous chemical reactions taking place in a closed system in the presence of a solvent.

Earth is a blue planet of the universe where water is an essential component. Circulation of water and other components such as entropy (energy) are driven by water vapor and heat (either external or internal). Water has a very important role in the formation of material or transformation of materials in Nature and the hydrothermal circulation has always been assisted by the bacterial activity. Hydrothermal processing as such is a part of the solution processing. It can be described as a superheated aqueous solution processing. Figure 1 shows the pressure–temperature map of various materials processing techniques (2). The solution processing is located in the pressure–temperature range characteristic for conditions of life on earth and the hydrothermal processing method becomes a part of this solution processing. All other processing routes are connected with increasing temperature and/or increasing (or decreasing) pressure. Therefore, they are environmentally stressed. Thus hydrothermal processing can be considered as environmentally benign. In the last decade, the hydrothermal technique has offered several advantages, eg, homogeneous precipitation using metal chelates under hydrothermal conditions, decomposition of hazardous and/or refractory chemical substances; monomerization of high polymers, eg, polyethylene terephthalate; and a host of other environmental engineering and chemical engineering issues dealing with recycling of rubbers and plastics instead of burning. The solvation properties of supercritical solvents are being extensively used for detoxifying organic and pharmaceutical wastes and also to replace toxic solvents commonly used for chemical synthesis. Similarly, it is used to remove caffeine and other food-related compounds selectively. In fact, the food and nutrition experts in recent years are using a new term *hydrothermal cooking*. These unique properties take the hydrothermal technique altogether in a new direction for the twenty-first century and one can forecast a slow emergence of a new branch of science and technology for sustained human development. The important topics of technology in the twenty-first century are predicted to be the balance of environmental and resource and / or energy problems. This has led to the development of a new concept related to the processing of advanced materials, viz, *industrial ecology*: science of sustainability (3).

During the twenty-first century, hydrothermal technology on the whole will not be limited to crystal growth, or leaching of metals, but it is going to take a very broad shape covering several interdisciplinary branches of science. Therefore, it has to be viewed from a different perspective. Further, the growing interest to enhance hydrothermal reaction kinetics using microwave, ultrasonic, mechanical, and electrochemical reactions will be distinct (4). Also, duration of the experiments is being reduced by at least two to four orders of magnitude, which in turn makes the technique more economic. With an ever-increasing demand for composite nanostructures, the hydrothermal technique offers a unique method for coating of various compounds on metals polymers and ceramics, as well as fabrication of powders or bulk ceramic bodies.

From the above statements, it is clear that hydrothermal processing of advanced materials is a highly interdisciplinary subject and the technique is

popularly used by physicists, chemists, ceramists, hydrometallurgists, materials scientists, engineers, biologists, geologists, technologists, etc. Figure 2 shows various branches of science either emerging from the hydrothermal technique or closely linked with it. One could firmly say that this family tree will keep expanding its branches and roots in the years to come.

The first successful commercial application of hydrothermal technology began with mineral extraction or ore beneficiation in the nineteenth century. The use of sodium hydroxide to leach bauxite was invented in 1892 by Karl Josef Bayer (1871–1908) as a process for obtaining pure aluminum hydroxide, which can be converted to pure Al_2O_3 suitable for processing the metal (5). Even today, 90 million tons of bauxite ore is treated annually by this process (6). Similarly, ilmenite, wolframite, cassiterite, laterites, a host of uranium ores, sulfides of gold, copper, nickel, zinc, arsenic, antimony, etc, are treated by this process to extract the metal. The principle involved is quite simple and very effective and inexpensive, eg,

$$Al(OH)_3 + OH^- \rightarrow [AlO(OH)_2]^- + H_2O$$
$$AlOOH + OH \rightarrow [AlO(OH)_2]$$
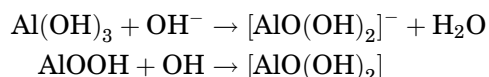
This process is easy to achieve and the leaching can be carried out in a few minutes at $\sim 330°C$ and 25,000 kPa (7).

Further, the importance of the hydrothermal technique for the synthesis of inorganic compounds in a commercial way was realized soon after the synthesis of large single crystals of quartz by Nacken (1946) and zeolites by Barrer (1948) during 1940s (8,9). The sudden demand for large size quartz crystals during World War II, forced many laboratories in Europe and North America to grow large crystals. Subsequently, the first synthesis of zeolite that did not have a natural counterpart was carried out by Barrer, in (1948) and this opened an altogether new field of science, viz, *molecular sieve technology* (10). The success in the growth of quartz crystals has provided further stimulii for hydrothermal crystal growth.

In any hydrothermal system or reaction, the role played by the solvent under the action of temperature and pressure is very important. It has been interpreted in various ways by many workers. Yoshimura and Suda (1994) (11) described the action of the hydrothermal fluid on solid substances under elevated pressure and temperature conditions and it is represented in Table 1.

Through proper interpretation of the above listed processes, one can easily develop the required hydrothermal processing using a suitable solvent to increase the solubility of the desired compound. Water is the most important solvent and it was popularly used as a hydrothermal mineralizer in all the earlier experiments. However, several compounds do not show high solubility for water even at supercritical temperature. Hence, the size of the crystals or minerals obtained in all the earlier hydrothermal experiments of the nineteenth century did not exceed thousandths or hundredths of a millimeter. Similarly, the time required for the processing of materials has longer durations. Therefore, the search for other suitable mineralizers began in the nineteenth century itself. A variety of aqueous and nonaqueous solutions were tried to suit the preparation of

a particular compound. The knowledge acquired through the use of several new mineralizers has helped to implement this hydrothermal technique as an effective one in preparative chemistry. Table 2 shows the use of hydrothermal processing in various fields of materials synthesis or processing (11). Before going into the details, it is appropriate to discuss natural hydrothermal systems.

2. Natural Hydrothermal Systems

The beginning of hydrothermal research is firmly associated with the study of natural systems by earth scientists, who were interested in understanding the genesis of various rocks, minerals, and ore deposits through laboratory simulations of the conditions existing in the earth's crust. During the nineteenth century, much of the hydrothermal work was confined to mineral synthesis, particularly silicate minerals. In fact, some even included this hydrothermal technology as a part of *silicate technology*. More recently, Japanese researchers are discussing a new concept, viz, *geothermal reactor*. The principles of a geothermal reactor include the direct use of geothermal energy as a heat source or driving force for chemical reactions. It helps to produce hydrothermal synthesis of minerals and a host of inorganic materials, extraction of useful chemical elements contained in crustal materials, such as basalt, and use them as raw materials for hydrothermal synthesis. Thus, the concept of a geothermal reactor leads to the construction of a high temperature and pressure autoclave underground. This has several advantages over conventional autoclave technology. The main disadvantage of the geothermal reactor is that the flow characteristics of a high temperature slurry accompanied by a chemical reaction must be well understood for controlling the reaction. The volumetric capacity of the geothermal reactor is very large compared to that of a usual autoclave, and the operation must be continuous. The merit of the geothermal reactor and its operational cost can be realized only if the target material is to be developed in large quantities (12).

   The spectacular nature of the submarine hydrothermal ecosystem with features, such as *"black smokers"*, *"white smokers"*, and peculiar ecosystems that are independent of sunlight as a source of reducing power, has focused much interest on hydrothermal processes for the explanation of an array of geochemical processes and phenomena (13). The submarine hydrothermal systems reveal that most primitive organisms found in modern environments are thermophiles (eg, *archea*). Many scientists believe in a "redox neutral" in the primitive atmosphere. The most important aspect is the possibility that iron vapor and reduced carbon liberated from impacting objects like meteorites would leave the ocean reducing for a long period. In addition, those submarine hydrothermal systems are the only environments where primitive life would have been protected against postulated meteoritic impacts and partial vaporization of the ocean. The presence of supercritical fluids, such as H_2O, CO_2, or CH_4, are the main constituents of any hydrothermal system. They serve as excellent solvents of organic compounds and would probably be of great potential for several of the chemical reactions eventually leading to the origin of life. Further, the pressure and

temperature gradients existing in natural hydrothermal systems have a dramatic effect on the properties of the hydrothermal fluids.

There are several reports on the laboratory hydrothermal synthesis of amino acids to justify the origin of life on earth. It is appropriate to mention that the organic synthesis on the whole is not new, and in fact, it began in the nineteenth century. However, the organic synthesis under hydrothermal conditions with reference to the origin of life began in a systematic way only during the 1980s, after the discovery of hydrothermal activity in the deep sea on a Galapagos spreading rich in thermophile organisms in 1977. Additional information can be found in Refs. 14–16. These workers synthesized amino acids in a temperature range of 150–275°C from aqueous solutions containing KCN, NH_3, HCHO, CO_2, H_2, O_2, CaC_2, NaCN, and NH_4HCO_3 solutions. Recently, based on thermodynamic calculations, Amend and Shock (1988) showed that the autotrophic synthesis of all 20 protein-forming amino acids was energetically favored in hot (100°C), and moderately reduced submarine hydrothermal solutions relative to their synthesis in cold (18°C), oxidized, surface sea water (17). Although these studies do not support the challenge raised by several others over life in submarine hydrothermal ecosystems, they definitely have set a new trend in hydrothermal research related to biological science.

3. Physical Chemistry of Hydrothermal Processing of Advanced Materials

Physical chemistry of hydrothermal processing of materials is perhaps the least known aspect in the literature. The Nobel symposium organized by the Royal Swedish Academy of Sciences in 1978, followed by the First International Symposium on hydrothermal reactions organized by the Tokyo Institute of Technology in 1982, helped in setting a new trend in hydrothermal technology by attracting physical chemists in large numbers (18,19). Hydrothermal physical chemistry today has enriched our knowledge greatly through a proper understanding of hydrothermal solution chemistry. The behavior of the solvent under hydrothermal conditions dealing with aspects, such as structure at critical, supercritical, and subcritical conditions; dielectric constants; pH variation; viscosity; coefficient of expansion; and density, are to be understood with respect to the pressure and temperature. Similarly, the thermodynamic studies yield rich information on the behavior of solutions with varying pressure–temperature conditions. Some of the commonly studied aspects are solubility, stability, yield, dissolution–precipitation reactions, etc, under hydrothermal conditions. Hydrothermal crystallization is only one of the areas where our fundamental understanding of hydrothermal kinetics is lacking due to the absence of data related to the intermediate phases forming in solution. Thus our fundamental understanding of hydrothermal crystallization kinetics is at an early stage, although the importance of the kinetics of crystallization studies was realized with the commercialization of the synthesis of zeolites during the 1950s and 1960s. In the absence of predictive models, we must empirically define the fundamental role of temperature, pressure, precursor, and time on the crystallization

kinetics of various compounds. Insight into this would enable us to understand how to control the formation of solution species, solid phases, and the rate of their formation. In recent years, the thermochemical modeling of chemical reactions under hydrothermal conditions is becoming very popular. Thermochemical computation data helps in intelligent engineering of the hydrothermal processing of advanced materials. The modeling can be successfully applied to very complex aqueous electrolyte and non-aqueous systems over wide ranges of temperature and concentration, and is widely used in both industry and academia. For example, OLI Systems Inc. provides the software for such thermochemical modeling, and using such a package of aqueous systems can be studied within the temperature range $-50-300°$C, with pressure ranging from 0 to 1500 bar, and concentrations from $0-30$ mm molal ionic strength. For the non-aqueous systems, the temperature range covered is from 0 to $1200°$C and the pressure is from 0 to 1500 bar with species concentration from 0 to 1.0 mol fraction.

A key limitation to the conventional hydrothermal method has been the need for time-consuming empirical trial and error methods as a mean for process development. Currently, the research is focused on the development of an overall rational engineering-based approach that will speed up process development. The rational approach involves the following four steps:

1. Compute thermodynamic equilibria as a function of chemical processing variables.
2. Generate equilibrium diagrams to map the process variable space for the phases of interest.
3. Design hydrothermal experiments to test and validate the computed diagrams.
4. Utilize the processing variables to explore opportunities for control of reaction and crystallization kinetics.

Such a rational approach has been used quite successfully to predict optimal synthesis conditions for controlling phase purity, particle size, size distribution, and particle morphology of PZT, hydroxyapatite (HAp), and other related systems (20,21). The software algorithm considers the standard-state properties of all system species as well as a comprehensive activity coefficient model for the solute species. Table 3 gives the example of thermodynamic calculations and the yield of solid and liquid species outflows at $T = 298$ K, $P = 1$ atm, $I = 0.049$ m, pH 12.4.

By using such a modeling approach, theoretical stability field diagrams (also popularly known as the yield diagrams) are constructed to get 100% yield. Assuming the product is phase pure, the yield Y can be expressed as

$$Y_i = 100(m_1^{\mathrm{ip}} - m_1^{\mathrm{eq}})/m_1^{\mathrm{ip}} \%$$

Where m^{ip} and m^{ip} are the input and equilibrium molal concentrations, respectively, subsript i stands for the designated atom. Figures 3 and 4 show the stability field diagrams for the PZT and HAp systems.

From Fig. 3, it is observed that the region with vertical solid lines represents the 99% yield of PZT although PZT forms within a wide range of KOH and Ti concentrations. This figure illustrates clearly the region where all the solute species transform toward 100% product yield. Similarly, from Fig. 4 it is observed that all the Ca species participate in the reaction to form HAp, thus leading to a 100% yield of HAp in the a. Thick dotted lines indicate the boundary above which 99% Ca precipitates as HAp. The other regions mark the mixed-phase precipitation, such as HAp, monatite, and other calcium phosphate phases.

Such thermodynamic studies help to intelligently engineer hydrothermal processing and obtain a maximum yield for a given system. This area of research has great potential application in materials processing.

4. Apparatus Used in Hydrothermal Processing of Materials

Materials processing under hydrothermal conditions requires a pressure vessel capable of containing highly corrosive solvent at high temperature and pressure. Hydrothermal experimental investigators require facilities that must operate routinely and reliably under extreme pressure–temperature conditions. Often, they face a variety of difficulties, and even some peculiar problems pertaining to design, procedure, and analysis. Designing a suitable or ideal hydrothermal apparatus popularly known as an autoclave, reactor, pressure vessel, or high pressure bomb, is a difficult task and perhaps impossible to define, because each project has different objectives and tolerances. However, an ideal hydrothermal autoclave should have the following characteristics:

1. Inertness to acids, bases, and oxidizing agents.
2. Easy to assemble and dissemble.
3. A sufficient length to obtain a desired temperature gradient.
4. Leak-proof with unlimited capabilities to the required temperature and pressure.
5. Rugged enough to bear high pressure and temperature experiments for a long time, so that no machining or treatment is needed after each experimental run.

Keeping these requirements in mind, the autoclave fabrication is done using a thick glass cylinder, thick quartz cylinder, high strength alloys [such as 300 series (austenitic) stainless steel], iron, nickel, cobalt-based super alloys, and titanium and its alloys. Here, it is impossible to describe all of the autoclaves design and working principles. Instead, it is prefered to describe only a few selected and commonly used autoclaves in the hydrothermal processing of materials. Table 4 lists the commonly used autoclaves along with their pressure–temperature limitations.

While selecting a suitable autoclave, the first and foremost parameter is the experimental temperature and pressure conditions and their corrosion resistance in that pressure–temperature range in a given solvent or hydrothermal

fluid. If the reaction takes place directly in the vessel, the corrosion resistance is of course a prime factor in the choice of autoclave material. In some of the experiments, the autoclaves do not insist on any lining, liners, or cans. For example, the growth of quartz can be carried out in low carbon steel autoclaves. The low carbon steel is corrosion resistant in systems containing silica and NaOH, because, the relatively insoluble NaFe−silicate forms and protectively coats the ground vessel. In contrast, the materials processing from the aqueous phosphoric acid media or other highly corrosive media like extreme pH conditions, then it requires a Teflon lining, beakers, platinum tubes, or lining to protect the autoclave body from the highly corrosive media. Therefore, the corrosion resistance of any metal under hydrothermal conditions is very important. For example, turbine engineers have long known that boiler water with pH >7 is less corrosive than slightly acidic water, especially for alloys containing silicon. Table 5 gives a list of the materials used as reactor linings (22).

Figures 5 and 6 show the most popular autoclaves designs, such as General Purpose, Morey, modified Bridgman, and Tuttle-Roy autoclaves. In most of these autoclaves, pressure can be either directly measured using the Bourdon gauge fixed to the autoclaves, or it can be calculated using PVT relations for water proposed by Kennedy (1950) (23). Figure 7 shows PVT relations in the $SiO_2−H_2O$ system.

These hydrothermal autoclaves can be used for a variety of applications, such as materials syntheses, crystal growth, phase equilibria study, hydrothermal alteration, reduction, structure stabilization, etc. There are several new autoclave designs commercially available, which are popularly known as the stirred autoclaves or reactors. Figure 8 shows the popular make of a stirred autoclave commonly used in hydrothermal materials processing. These reactors have special features, eg, the reactor contents can be continuously stirred at different rates, the fluids can be withdrawn while running the hydrothermal experiment, and the desired gas can be supplied externally into the reactors. Such features help greatly to withdraw the fluids from time to time and are subject to various analytical techniques to determine the intermediate phases, which facilitate the understanding of the hydrothermal reaction mechanism for a given material preparation.

There are many more reactor designs for special purposes such as rocking autoclaves, PVT apparatus, multichamber autoclaves, fluid sampling autoclaves, microautoclaves, autoclaves for visual examination, hydrothermal hot pressing, vertical autoclaves, continuous flow reactors, hydrothermal electrochemical autoclaves, autoclaves for solubility measurements, autoclaves for kinetic study, pendulum autoclave, horizontal autoclaves for controlled diffusion study, etc. The reader can find details of the construction and working mechanisms of these autoclaves from the source (1).

Safety and maintenance of the autoclaves is the prime factor to keep in mind in carrying out experiments under hydrothermal conditions. It is estimated that for a 100-cm^3 vessel at 20,000 psi, the stored energy is ~15,000 foot-1b. The hydrothermal solutions—either acidic or alkaline—at high temperatures are hazardous to humans, if the autoclave explodes. Therefore, the vessels should have rupture disks calibrated to burst above a given pressure. Such rupture disks are commercially available for various ranges of bursting pressure. The

most important arrangement is that provision should be made for venting the live volatiles out in the event of rupture. Proper shielding of the autoclave should be given to divert the corrosive volatiles away from personnel. In the case of a large autoclave, the vessels are to be placed in a pit with proper shielding.

5. Hydrothermal Crystal Growth of Quartz and Related Materials

The hydrothermal technique is the only mean of producing the most important piezoelectric material, such as α- quartz, which is one of the most extensively studied materials. The principal source of electronic grade natural quartz is Brazil. Today the electronic industries are largely inclined to use synthetic quartz, because natural quartz crystals are generally irregular in shape, automatic cutting is cumbersome, and the yield is low. Over 3000 tons of quartz is produced annually for a variety of applications. The cost involved in the production of quartz is as follows:

End users	~US$1,000,000,000,000
Equipment	~US$5,000,000,000
Components	~US$1,00,000,000

Thus quartz takes first place in value and quantity of single-crystal piezoelectric materials produced by humans (24).

In the growth of α- quartz by the conventional method, the autoclaves used by most of the workers were modified Bridgman types of autoclaves. The typical laboratory size autoclave is 1 inch diameter × 1 ft length. The pressure autoclave used in Europe and The United States is the "13 inch" diameter and >10 ft—length autoclave with 350-L internal volume. This autoclave gives some 150 kg of quartz per cycle. But an evolution concerning the vessel's dimensions has to be noted, especially in Japan, where autoclaves with 1000–5000 L of internal volume are in operation producing 500–5000-kg quartz per cycle. Figure 9 shows the internal assembly of the modified Bridgman autoclave used popularly in the growth of quartz crystals (25).

In the growth of α- quartz, available nutrient material such as small particle size α- quartz, silica glass, high quality silica sand, or silica gel is placed in a liner made up of iron or silver with a suitable baffle and a frame holding the seed plates. A mineralizer solution with a definite molarity is poured into the liner to make the required percent fill.

The optimum growth conditions for synthesis of quartz based on the work from Bell Laboratories are (25):

dissolution temperature	425°C
growth temperature	375°C
pressure	15,000–25,000 psi
mineralizer concentration	0.5–1.0 M NaOH
temperature gradient (DT)	50°C
% fill	78–85%
growth rate in (0001)	1.0–1.25 mm/day

The quality of the grown crystals is also a function of the seed orientation and its quality. Strained seeds generally produce strained growth regions. Most high quality crystals are grown using seeds, the surface of which is perpendicular to the Z direction, since the Z-growth region is the lowest in aluminium concentration. Though the main part of quartz production consists of "*Y bar*" crystals, ie, small crystals ($Z = 20$–25 mm, 64-mm seed) capable of several Y bars/crystal, the "*pure Z*" bars are also produced representing 10–20% of this production. But in medium and high quality grades we notice a rise in demand for crystals of very large dimensions and upper medium quality, especially in the United States, for manufacturing wafers used in surface wave applications (26). Earlier, most of the seeds used were natural quartz cut into a definite orientation, but in recent years this practice is only used when a high quality crystal is desired.

The growth of quartz crystals has been understood precisely with reference to the growth temperature, temperature gradient, and percent of fill, solubility, percent of baffle opening as a function of percent of fill.

The type of crystal to be grown depends on the application, as different properties are required in each case. The more precise the need, the more stringent are the requirements. For most applications, a truly high quality material is not needed. For high precision uses, such as in navigational devices and satellites, a very high quality material must be used. Most of the recent research on quartz growth is for improved resonator performance, which requires the growth of high quality, and low dislocation quartz. Figure 10 shows the growth of quartz crystals using the world's largest autoclave in Japan.

Several criteria are used to evaluate the quality of quartz crystals. The most commonly used criterion is the Q value or quality factor, and is a measure of the acoustic loss of the material. The acoustic Q for natural α-quartz crystal varies in the range 1–3×10^6, while for synthetic quartz crystals, the value drops down to 2.105–1.106. Thus in the last two decades, the main objective among quartz crystal growers is to improve Q, which in turn leads to the production of a low concentration of physicochemical and structural defects.

In comparison with α-quartz, there are two more materials like berlinite and gallium phosphate, which are also produced hydrothermally. Table 6 shows the comparison of the properties of these three piezoelectric materials. However, there are problems associated with the growth of these two materials as bulk crystals owing to their negative solubility and the highly corrosive nature of the phosphorus media, which attacks the liners and the autoclave body.

The growth of berlinite and gallium phosphate is carried out using the experimental conditions given below:

growth temperature	170–240°C
pressure	15–35 MPa
solvents	usually mixed-acid mineralizers
liners	Teflon liners
nutrient	powered nutrient, preferably respective glasses
horizontal temperature difference	$5 < T < 30$°C
filling	80%
growth rate	0.35–0.50 mm/day in H_3PO_4
	0.35–0.45 mm/day in HCl
	0.25–0.35 mm/day in HNO_3
	0.2–0.3 mm/day in H_2SO_4

On the whole, the quality of the crystals grown and the growth rate depend on the solvent, solvent concentration, growth temperature, type of nutrient, seed orientation, and temperature gradient. Figure 11 shows hydrothermally grown crystals of $GaPO_4$ and $AlPO_4$.

In recent years, there has been a growing interest in the hydrothermal growth of gallium nitride crystals. The energy difference between the valence and conducting energy bands in GaN make it an attractive material for photonic and electronic devices. Gallium nitride laser diodes offer over a sixfold increase in storage capacity for the next generation of DVDs, while gallium nitride LED-based illumination sources are replacing less energy efficient lighting. Further, transistors made from gallium nitride exhibit 10–100 times the power capacity as transistors made of silicon or gallium arsenide. However, there is a major problem related to the production of high quality GaN crystals from conventional techniques, such as the melt or physical vapor deposition techniques that are uneconomical and reliable because of the high volatility of gallium nitride.

Supercritical ammonia (*sc*) solution growth of bulk gallium nitride has the promise of producing high quality nitride crystals through the application of techniques similar to hydrothermal growth. The similarities in equipment, chemistry, and physical driving forces give useful insight into the design of experiments using high nickel content autoclaves, at pressures 1–3 kbars and temperatures between 300 and 600°C. Gallium nitride shows retrograde solubility and >5% by weight can be achieved when using group I amides as mineralizers. Gallium nitride hydride vapor-phase epitaxy (HVPE) seeds are placed in the higher temperature zone below the nutrient basket in much the same way as the hydrothermal growth of berlinite ($AlPO_4$). Pressure is varied, depending on the amounts of ammonia, mineralizer, and other volatile species in the system. Growth rates under these conditions have been up to 40-μm/day on 1-cm^2 seeds. Though numerous experiments yielded varying crystalline quality, it is generally found that growth on the nitrogen face tends to exhibit better morphology, and up to twice the growth rate of the gallium face (27). But the bulk

growth of defect free crystals of gallium nitride still needs a coherent research activity.

On the whole, there is a trend in the hydrothermal growth of crystals recently, and it is shown in Table 7.

Table 7 clearly indicates the change in the trend among the hydrothermal researchers to search for lower PT conditions for the growth of a variety of crystals with the help of thermochemical modeling and the hydrothermal chemistry of the media.

By using the hydrothermal technique, a wide variety of technologically important crystals, such as potassium titanyl phosphate (KTP), potassium titanyl arsenate, calcite, metal oxides, phosphates, tungstates, vanadates, and several gemstones, such as ruby, corundum, emerald, and colored quartz, have been grown both as bulk and small crystals (1). The method facilitates the growth of more perfect crystals with a lesser degree of defects.

6. Hydrothermal Synthesis of Advanced Inorganic Materials

This section presents the hydrothermal preparation of zeolites and other advanced inorganic materials. The hydrothermal processing of ceramics will be discussed separately in Section 8. The hydrothermal technique has proved its efficiency in the synthesis of a great variety of inorganic materials like zeolites, complex coordinated compounds with mixed-framework structures covering a wide range of silicates, phosphates, vanadates, arsenates, molybdates, tungstates, fluorides, sulfates, selenides, borates, etc. The process of their formation under hydrothermal conditions although in some cases is slower, leads to phase purity, tight control over their morphology, size, and incorporation of special physical and chemical properties, which is not possible in the other conventional techniques.

6.1. Zeolites. Zeolites form an important group of hydrated aluminosilicate minerals of the alkalies and alkaline earths, with an infinitely three-dimensional (3D) anion network, and with the atomic ratio O: (Al + Si) = 2. Zeolite structures contain larger cavities–channels and therefore, many exhibit the properties of ion exchange and molecular adsorption. Further, these cavities or channels in zeolites are usually filled with water molecules. These are relatively loosely bound to the framework and cations, and like the cations, these can also be removed and replaced without disrupting framework bonds. McBain (1954) introduced a new term "*molecular sieve*" to zeolites to describe porous materials that can act as sieves on a molecular scale and are not just limited to aluminosilicate zeolites, but to a large number of other zeolites like alumniophosphate zeolites, vanadophosphate zeolites, titanophosphate zeolites, etc (28). The zeolites and related materials, such as phosphate-based molecular sieves are microporous solids with a broad range of physicochemical properties.

Efforts to synthesize zeolites could be traced as far back as 1848, when Wöhler first recrystallized apophyllite by heating apophyllite in water solutions at 180–190°C under 10–12 atm (29). Followed by this, several more attempts were made during the 1860s, when Claireville synthesized zeolites by the hydrothermal method in 1862 (30). The hydrothermal reaction merges into a low

temperature reaction and indeed, in zeolite synthesis the trend has been inter alia for greater experimental convenience, to grow zeolites at or below 100°C provided reaction rates are adequate. It is only during the 1940s that great attention was devoted to the zeolite synthesis, as a result of the poineering work by Barrer, and co-workers (31,32). The zeolite synthesis is shown schematically in Fig. 12.

Even now, the area of zeolite synthesis is still expanding, and hence is resulting in the discovery of synthetic zeolites with new topologies and new catalytic sorption and separation properties. Generally, three processes are used to produce zeolites. All three processes utilize hydrothermal conditions:

1. Preparation of molecular sieve zeolites as high purity crystalline powders.
2. The conversion of clay minerals into zeolites.
3. Processes based on the use of other naturally occurring raw materials.

In the zeolite synthesis, one has to carefully monitor each step in order to prepare a desired zeolite phase with reproducibility. This covers gel preparation, gel pretreatment, gel aging, pH of the media, experimental duration, experimental temperature of the synthesis, molar proportions of the starting material, type of organics, the time of addition of organics, and the alumina source play an important role. The aluminosilicate zeolites are crystallized in a strong basic medium with the pH of the reaction mixture >13, but for the successful crystallization of aluminophosphate zeolites, the pH range of the hydrous gel has to be in the range of 3.5−6.0. A slight change in any of these parameters largely influences the resultant product.

There is a growing interest in the development of inorganic films and membranes with controllable porosity owing to their promising applications in asymmetric membranes, catalytic monoliths, and chemical sensors (34). The interest in microporous thin films is primarily motivated by their potential molecular sieving action, large surface areas, and controlled host−sorbate interacts, especially at low vapor pressures. Similarly, zeolites also have been embedded into polymers, covered with glazes, and extruded into composite monoliths (35).

Conventional applications of zeolites are adsorptive, gas separation, shape-selective catalysis, and ion exchange. In recent years, there has been an increased research activity in molecular sieve science and technology toward the development of advanced materials. There are several reports available in the literature dealing with the controlled incorporation of guest compounds into a zeolitic framework to get new optical, electronic, and magnetic materials, such as intrazeolite sulfides; selenides, silver compounds; carbonyls; the intra-crystallization polymerization of acetylene and pyrrole; the formation of metal clusters; and trapped supramolecular compounds (ship-in-one-bottle) (36).

On the whole, the zeolite synthesis involves considerable trial and error in the design of a chemical process for a zeolite having specific properties. The synthesis is carried out under subcritical water temperatures and pressures using batch reactors. The experimental duration lasts several hours or up to several days depending on the process and product composition. However, the recent microwave hydrothermal has significantly reduced the reaction time for zeolite formation.

7. Hydrothermal Processing of Advanced Ceramics

The term advanced ceramics processing usually refers to the hydrothermal technique. Most of the ceramic oxide powders are made by a ball-milling and calcination processes resulting in the formation of less dense and uncontrolled particle distribution. This section covers the hydrothermal processing of most popular electronic ceramics, such as PZT, bioceramics, the epitaxial growth of crystalline thin films, composites, and ultrafine particles with a desired shape and size.

The hydrothermal technique is ideal for the processing of very fine powders having high purity, controlled stoichiometry, high quality, narrow particle size distribution, controlled morphology, uniformity, less defects, dense particles, high crystallinity, excellent reproducibility, controlling of microstructure, high reactivity–sinterability, etc. Further, the technique facilitates issues, such as energy saving, use of a large volume of equipment, better nucleation control, pollution free, higher dispersion, high rate of reaction, better shape control, and low temperature operation in the presence of the solvent. In nanotechnology, the hydrothermal technique has an edge over the other materials processing technologies, since it is ideal for the processing of designer particulates. The term designer particulates refers to the particles with high purity, high crystallinity, high quality, monodispersion, and showing the desired physical and chemical characteristics. Today, such particles are in great demand in the industry. Figure 13 shows the major differences in the products obtained by ball milling or sintering or firing and hydrothermal methods. Currently, the annual market value of electronic ceramics is >\$1 billion.

Of all the electronic ceramics, the PZT family of ceramics has been studied extensively. From the early 1980s, thousands of reports have appeared on the preparation of these ceramics. Riman and his group have done excellent work on the preparation of these PZT type of ceramics and have studied in detail the thermodynamics and kinetics of these systems (20,21). 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 approach this problem from a multidisciplinary perspective of chemistry, chemical engineering, and physical chemistry, which all embrace the principles of thermodynamics and kinetics (37). 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 hydrothermal medium, more of a typical PZT system, eg, in the Ba–Ti and Pb–Ti systems. Figure 3 shows the calculated stability field diagram for the PZT system. The exact processing conditions and the precursor compositions can be selected by using such a diagram. Also, the group has done good work in the area of size and morphology control by using such thermodynamic data. Figure 14 shows the designer particles prepared under hydrothermal conditions. The stability diagrams were considered for a limited number of hydrothermal systems on the assumption that the aqueous solutions were ideal (37,38). It is 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 and yield diagrams also help greatly in the hydrothermal synthesis of phase-pure ceramics.

The majority of the PZT systems incorporate intolerable amounts of alkaline metals, which are introduced in the form of mineralizers. In recent years, organic mineralizers were being used by a large number of workers. For example, Riman (1996) found that tetramethylammonium hydroxide, $N(CH_3)_4OH$, is a favorable substitute for alkaline metal hydroxide mineralizers in producing phase-pure PZT (31). Phase-pure $MTiO_3$ (M $=$ Ca,Sr,Ba) can be obtained at input molalities of Ba, Sr, and Ca $>7 \times 10^{-5}$, 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:

$$Me^{2+} + TiO_2 + 2OH^- = MeTiO_3 + H_2O$$

Such an approach to understand the crystallization mechanism of the PZT family of materials has been made by several workers from all around the world, and there are many commercial producers of these ceramics especially in United States, Japan, and Europe.

Several other oxides, such as ZrO_2, CeO_2, SnO_2, SrO, and CaO, are doped into the structures of perovskite-type electronic ceramics to improve electrical properties, such as dielectric permittivity, dielectric loss, etc.

The hydrothermal technique is also popularly used in the synthesis of TiO_2 and related metal oxide powders, such as ZnO, Fe_3O_4, SnO_2, α-MnO_2, etc. Among these, TiO_2 is the most extensively studied material owing to its unique heterogeneous photocatalytic properties. It is nontoxic and chemically inert. Several organic pollutants present in industrial waste waters, phenol, nitrophenol isomers, and their derivatives, aromatic hydrocarbons, cyanide, sulfites, etc., have been completely removed by using this TiO_2-based heterogeneous photocatalysis. Several authors have studied in detail the hydrothermal synthesis of TiO_2 particles and the influence of various processing parameters, such as temperature, experimental duration, pressure (percentage fill), solvent type, pH, and the starting charge on the resultant product. The following experimental conditions are used for the preparation of monodispersed ultrafine particles of TiO_2:

nutrient	preheated anatase phase or Ti gel
temperature	150°C
duration	6–40 h
pH	2
% fill	60%
mineralizer	1.5 M HCl

The size and morphology of the TiO_2 particulates play a significant role in the applications. Figures 15 and 16 show the TiO_2 and ZnO particulates

prepared under hydrothermal conditions. Further, it is observed from the litera-
ture data that hydrothermal techniques offer advantages to control the size and
shape of these particulates. The preferred shape of the particles is spherical to
subspherical, with the particle size up to 100 nm. Such a small particle size
gives higher surface area and higher reactivity for the photocatalyst.

   7.1. Hydrothermal Processing of Advanced Bioceramics.   Bioicera-
mics represent a broad spectrum of ceramic materials designed for chemical com-
patibility and optimal mechanical strength with the physiological enviroment.
Bioceramics may be bioinert (alumina, zirconia), resorbable (tricalcium phos-
phate), bioactive (hydroxyapatite, bioactive glasses, and glassceramics), or por-
ous for tissue in growth (HAp coated metals, alumina). Applications include
replacements for hips, knees, teeth, tendons, and ligaments as well as repair
of periodontal disease, maxillofacial reconstruction, augment and stabilization
of the jawbone, spinal fusion, and bone fillers after tumor surgery (39).

   High density, high purity (>99.5%) Al_2O_3 (α-alimina) was the first biocera-
mic 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 biocompatibility, low friction, high wear resistance, and high
strength (40). Zirconia (ZrO_2), in tetragonal form, stabilized by either magne-
sium or yttrium, also has been developed as a medical-grade bioceramic for
use in total joint prostheses. These materials are prepared by hydrothermal tech-
niques, such as hydrothermal sintering, hydrothermal hot pressing, and under
hot isostatic pressure.

   The most significant bioceramics of today are a more complex material:
HAp, $Ca_{10}(PO_4)_6(OH)_2$, which is the main mineral constituent of teeth and
bones representing 43% by weight. It has the physicochemical advantages of sta-
bility, inertness, and biocompatibility. The HAp ceramics do not exhibit any
cytoxic effects, and HAp can directly bond to bone. Unfortunately, due to low
reliability, especially in wet environments, HAp ceramics cannot be used for
heavy load-bearing applications, such as artificial teeth or bones. Nevertheless,
there has been a lot of research aimed at fabricating more mechanically reliable
bioactive ceramics including, the HAp materials. Suchanek and Yoshimura
(1998) reviewed in detail the past, present, and future of the HAp-based bioma-
terials from the point of view of preparation of hard tissue replacement implants
(41). 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^{2-}_3, F^-, Cl^-, and H_2O. All these species, if applied in
appropriate quantities, should be well tolerated in the implant by the surround-
ing tissues.

   Presently, the hydrothermal processing of hydroxyapatite bioceramics is at
the pinnacle stage of its development. Hydrothermal powder processing, forma-
tion, and densification have been understood quite well, allowing for the control
of chemical composition and microstructures of both dense and porous HAp cera-
mics. The hydrothermally prepared HAp powders show whiskers, needles, or
small thick particles. Reduction of the aspect ratio is a major issue in the pre-
paration of HAp powders. Only in the hydrothermal method it is possible to

reduce the aspect ratio. Figure 17 shows the hydrothermally prepared HAp designer particulates using the stirring mechanism.

7.2. Hydrothermal Processing of Composites. The nature invented composites, wood (cellulose and lignin) and bone (the polymer collagen and the mineral hydroxyapatite), are the specific examples. A composite can and often does have much more desirable properties than the individual pure or virgin materials from which it was made. Tailoring the properties of the interface between reinforcing component and matrix is a major application of chemistry in improving the performance of composites. The surface treatments, now used to modify the surface properties of reinforcing fibers in composites, are largely empirical. In this regard, the hydrothermal method of processing the materials to obtain composites and multilayers of ceramics and coating of substrates on other materials is very significant.

Recently, film HAp has become important as a coating for metal or ceramic bodies, and tiny electronic devices such as sensors. Uncoated metal implants do not integrate with bone because, bioinert materials are encapsulated by dense fibrous tissue that prevent proper distribution of stresses, and thereby cause loosening of the implant. In the case of HAp, coated metal, bone tissue integrates itself completely with the implant, even during the early functional loading. Moreover, the HAp coatings decrease the release of metal ions from the implant to the body, and shield the metal surface from environmental attack. The HAp coatings have been applied to metals, such as Ti alloys or Ca−Cr−Mo alloy, to carbon implants, sintered ceramics, such as ZrO_2 and Al_2O_3, and even to polymers, poly(methyl methacrylate) (PMMA). There are various methods to fabricate HAp coatings. The common ones are HIP, spray-painting, oxy-fuel combustion spraying magnetron sputtering, flame spraying, ion-beam deposition, and chemical deposition under hydrothermal conditions, electrochemical deposit, metal-organic CVD, and sol−gel. The coating under hydrothermal conditions has been carried out effectively by many workers as the technique gives more uniform thickness and firm coating.

In recent years, there has been a growing tendency to impregnate the active metal oxides onto the surface layers of activated carbon to prepare a highly effective photocatalytic support-based composite for environmental issues. Preparation of such a composite increases the active sites for the reaction by bringing the reactant molecules close to the catalyst surface. The activated carbon has a high surface area and a well-developed porosity, which are essential for achieving large metal dispersions, giving high catalytic activity (42). The surface area and porosity available in the activated carbon is usually much larger than those in alumina or silica, and a large proportion of the surface area is contained within micropores. Hydrothermal technology has been efficiently used to impregnate TiO_2 or ZnO onto surface layers and the pores of activated carbon. Byrappa and co-workers (43) reported the impregnation of highly active and monodispersed designer particulates, such as TiO_2, onto activated carbon under mild hydrothermal conditions (T:<200°C and $P{\sim}30$ bars). The prepared TiO_2:AC / ZnO:AC composites have been used in the degradation of various hazardous environmental contaminants. Similarly, other interesting composite materials are the coatings of ZnO or Nd_2O_3 onto the TiO_2 particulates. When Nd_2O_3 or ZnO is coated onto the TiO_2, the efficiency of the prepared composites

(Nd_2O_3:TiO_2) increases. The hydrothermal experimental conditions used in the preparation of these hybrid particles are given below:

nutrient	commercially available activated carbon mixed with commercial TiO_2/ZnO or liquid precursors such as TTIP, $TiCl_4$, etc, and $ZnCl_2$ for ZnO
temperature	150–200°C
duration	6–24 h
% fill	60%
mineralizer	mild acids or alkali

Figures 18 and 19 show the TiO_2 and ZnO impregnated activated carbon hybrid particulates prepared using the hydrothermal method. The particles are monodispersed and spherical in shape.

These active metal oxides are chemically bonded with the activated carbon surface layers at the micropores with van der Waals bonds. Hence, repeated centrifugation and ultrasonication did not remove the active metal oxides from these activated carbon layers.

7.3. Related Methods of Hydrothermal Processing of Materials.

The modern methods of hydrothermal processing of materials cover several other processing techniques related to the hydrothermal method. Although these new methods are not used widely in routine hydrothermal processing, they have special applications in the processing of some selected technological materials, such as hydrothermal transformation, alteration, recycling, densification, solidification, strengthening, sintering, etc. The most commonly used processing techniques are HHP, HIP, hydrothermal sintering, microwave hydrothermal, hydrothermal leaching, hydrothermal decomposition of toxic organic materials, etc.

The HHP technique is a good processing route for preparing a ceramic body at relatively low temperatures (<300°C). The compression of samples under hydrothermal conditions accelerates densification of inorganic materials. This technique is applied to solidify many kinds of materials, such as glass, silicate, titania, calcium aluminate-phosphate cement, calcium carbonate, hydroxyapatite, sewage sludge, etc (44,45). This method is expected to provide energy-effective processing to fabricate new engineering materials. By using the HHP technique, the strength of solidified bodies with mixtures of alumina cement or calcium aluminates, sodium phosphates, and silica fume could be enhanced.

The HIP technique allows rapid densification with mineral grain growth and is one of the most effective ceramic densification processes. This method is being popularly employed to process HAp-based bioceramics (46). Implant materials require not only biocompatibility, but also mechanical strength and porosity to promote the connection with tissues. Therefore, microstructure designing, ie, grain size, pore size, and porosity, need to be tailored in the application as bioceramics. Hydroxyapatite single crystals ~255×90 nm in size were synthesized hydrothermally at 200°C under 2 MPa for 10 h and were sintered normally in air for 3 h. The ceramics obtained were hot isostatically pressed at temperatures of 900–1100°C under 200 MPa of Ar for 1 h without any capsules. This postsinter-

ing brought about densification up to ~100% for the samples >90% dense having closed pores. The fully dense ceramics with a grain size of ~0.54 μm showed transparency. Furthermore, dense–porous layered hydroxyapatite ceramics could be prepared by the same technique from the fine crystals and coarse powders with relatively low sinterability.

Microwave hydrothermal is a fast growing field of advanced materials processing. A wide range of materials, such as the perovskite family of ceramics, ferrites, zeolites, HAp, metal oxides, metal intercalated clays, etc, have been prepared by this technique. The microwave hydrothermal significantly accelerates the kinetics of reactions and exponentially reduces the time duration required for materials processing, which makes the process extremely fast and highly cost effective. Excellent reviews are available on this topic in the literature (47).

Hydrothermal epitaxy to prepare thin films is another area that is catching up fast in modern materials processing. It is popularly known as the hydrothermal-electrochemical technique, which is a very convenient method of preparing a wide range of films on the substrates, coating of materials, preparation of multilayered compounds, functionally gradient materials, etc (48). This method is especially versatile and convenient, because of the lower temperature and pressure conditions involved in contrast to the conventional hydrothermal technique involving very high pressure–temperature conditions. Among the compounds obtained through the hydrothermal-electrochemical technique, the perovskite type alkaline earth titanates dominate, followed by tungstates, molybdates, and a series of solid solutions of alkaline earth titanates (49).

7.4. Hydrothermal Treatment–Recycling–Alteration. This is probably one of the most important areas of research in the field of hydrothermal technology, wherein, the supercritical water (SCW) properties are exploited for effective detoxification and disposal of problematic industrial, nuclear, military, and municipal wastes. Although this technology developed during the 1970s and 1980s to meet the requirements of some corporate industries, today it has become a focal point in twenty-first century hydrothermal research. This technology was first commercialized by Modar (Natick, Massachusetts) and today there are several industries using this technology commercially worldwide. In SCW at 450–700°C, many organic compounds are rapidly (0.1–100s) and efficiently (99.9–99.99 + %) oxidized (supercritical water oxidation or SCWO), with their carbon, hydrogen, and nitrogen almost completely converted to CO_2, H_2O (mineralization), and N_2. These attributes make SCW an attractive medium for chemical reactions and physical separations, ie, for hydrothermal processing. Environmental applications include rapid and efficient destruction of hazardous organic substances, eg, aqueous wastes, and decontamination, and / or separation of inorganic pollutants. Thus, supercritical water oxidation is an emerging technology for the treatment of aqueous waste streams, so that they can be recycled as process streams and for the ultimate destruction of organic wastes. Recycling of waste plastics, such as polyethylene, polystyrene, polypropylene and polyethyleneterephthalate, radioactive waste, concrete wastes, etc, have received special attention. Similarly, the decomposition of chlorocarbons, chlorofluorocarbons, polymers, polymer additives, nitroaromatics, etc, under higher pressure–temperature conditions, have been well understood. The conventional method

of treating most of these waste materials is the oxidation pyrolysis in incinerators. But this method is not effective for the dechlorination of chlorofluorocarbons, eg, high temperature plazma destruction needs large and expensive apparatus and the reactors are easily corroded by HCl or Cl_2 gas (the decomposed productions). Similarly, reductive decomposition is not a cost-effective method because it requires expensive reductive agents (1).

Savage and co-workers worked out the reaction models for supercritical water oxidation processes in detail, based on molecular dynamics studies of supercritical water in order to understand better the potential roles of water in influencing elementary chemical reaction rates (50). The study of hydrogen bonding in supercritical water and its dependence on temperature and density has been carried out by many workers to understand fundamental issues connected with structure dynamics and thermodynamics of pure water (51).

Hydrothermal decomposition of organics, or recycling of waste materials, is usually carried out in small autoclaves, or Tuttle cold-cone seal autoclaves, or batch reactors–flow-reactors, depending on the experimental conditions and purpose.

Adschiri and co-workers (1994) studied the conversion of lignin, polystyrene, and polyethylene under supercritical conditions of water and found that polystyrene could be completely decomposed into ethylbenzene, toluene, benzene, styrene, and xylene in 5 min. However, the conversion yield of polyethylene was fairly low even at a longer reaction time of 2 h at 35 MPa, 400°C; but by the addition of oxygen ($\sim$0.013 mol), conversion increased to 60% at the same temperature. The advantages of such conversion are that lesser char and more aldehyde, ketone, and acid production in SCW are observed, as compared to neat pyrolysis reaction (52).

The above works clearly indicate that a new trend is being set in hydrothermal technology. This technology is going to be highly cost effective. Already, several groups have cropped up all over the world to tackle the existing problems and search for new avenues in materials synthesis and processing under a new concept called green materials and green processing, which deal with industrial ecology, environmentally friendly methods, recycling, etc.

Hydrothermal–solvothermal processing helps greatly in the structure stabilization of several new compounds (53). The natural phyllosilicates are characterized by a low thermal stability due to the presence of $(OH)^-$ groups in the lattice. Through hydrothermal treatment, the replacement of (OH) groups by oxygen atoms takes place, and this in turn improves the thermal stability of phyllosilicates. Similarly, the replacement of metals can be carried out under hydrothermal conditions to obtain new structures.

Recovery, recycling, decomposition, and treatment processes under hydrothermal conditions are going to play a major role in the twenty-first century. Figure 20 shows the author's imagination: a new generation complex industry constructed underground, which exhaust no toxic or hazardous waste (54). It is an ideal closed system by combination of waste treatment, energy recovery, and formation of resource. This deals with the recovery process of human waste to energy resource using hydrothermal technology. The authors have decomposed the night soil without any insecticides and deodorizers using hydrothermal technology. The decomposition of the night soil was defined by the ratio

of COD/Mn before and after the reaction. The decomposition ratio increased with increasing temperature, and oxygen pressure >2 MPa accelerated decomposition. The night soil was decomposed >90% when the conditions of hydrothermal treatment were at 300°C of reaction temperature for 10 min. Under these conditions, the hydrothermal decomposition of night soil occurred with the offensive smelling gas. In a future society, a closed system such as this type must be attained in all industry fields for survival of modern civilization and for earths ecology. To quote an example of such a system, at IAx Corp., Japan, a new closed system for collection of waste, separation, and recycling has been introduced and achieved a reduction in waste output by 85% without increasing the intake (Fig. 21).

In order to achieve the objective of waste zero system, the corporation is working out new technology based on the *"closed-manufacturing system"*. Soil solidified hydrothermally is a new material born from the development of a closed production system (55). The strength of the hydrothermally processed soil is equal to or greater than that of concrete building materials (flexural strength = 4–6 MPa). Its heat capacity is greater than that of wood flooring (1090 kJ/m^3 K), tatami (430 kJ/m^3 K), and carpet (330 kJ/m^3 K). It also exhibits high humidity absorption and desorption ability similar to wood, because of its pore sizes, which are extremely small (10–20 nm) compared to concrete blocks or conventional chinaware. Extremely small pores result from the pores in the raw material (soil) itself and the pores that are formed during hydrothermal solidification. This hydrothermally treated soil product with a trade name *Earth Ceramics*, is being widely used as flooring material in Japan because of the improved properties compared to conventional materials. The amount of energy used for air conditioning after the use of soil ceramics was 25% less than that without earth ceramics. Similarly, earth ceramics have fewer allergic problems than vinylon cloth and carpets. Thus, hydrothermal processing helps greatly in the production of ecofriendly materials, viz, ecomaterials or green materials. The processing can be called green processing of materials because it is environmentally benign.

8. Conclusions

Hydrothermal processing of advanced materials is an important branch of science and technology owing to its advantages over conventional technologies in terms of materials purity, quality, and performance, as well as its being environmentally friendly, since it consumes lesser energy and the reactions are carried out in a closed system. Hydrothermal processing covers a very broad range of processing techniques that are in use for a great variety of inorganic and organic materials preparation. To summarize, the recent trends in hydrothermal processing of materials covers the study of solvent chemistry, solubility, and solvent–solute interaction, complexation. Modeling of crystallization mechanisms and intelligent engineering of materials; soft hydrothermal technology for materials synthesis and processing; reduction in pressure and temperature; cost effective, environmentally benign processing; use of organic precursors; simple autoclave design; possibility of visual observation; synthesis

of new materials; hydrothermal electrochemical or film growth; hydrothermal synthesis of diamond; hydrothermal preparation of whiskers; hydrothermal synthesis of life-forming organics; hydrothermal microwave; hydrothermal mechanochemical; hydrothermal sonochemical; hydrothermal recycling; hydrothermal with selective gas systems; hydrothermal nanotechnology; continuous processing of materials (flow reactors, closed system, solvothermal recycling); hydrothermal treatment (alteration, extraction, etc); hydrothermal crystal synthesis and growth of bulk crystals; hydrothermal preparation of fine crystals with controlled size, shape, and composition; hydrothermal sintering with or without reactions; hydrothermal etching; hydrothermal corrosion; etc. Thus, hydrothermal technology has moved significantly from geology to technology.

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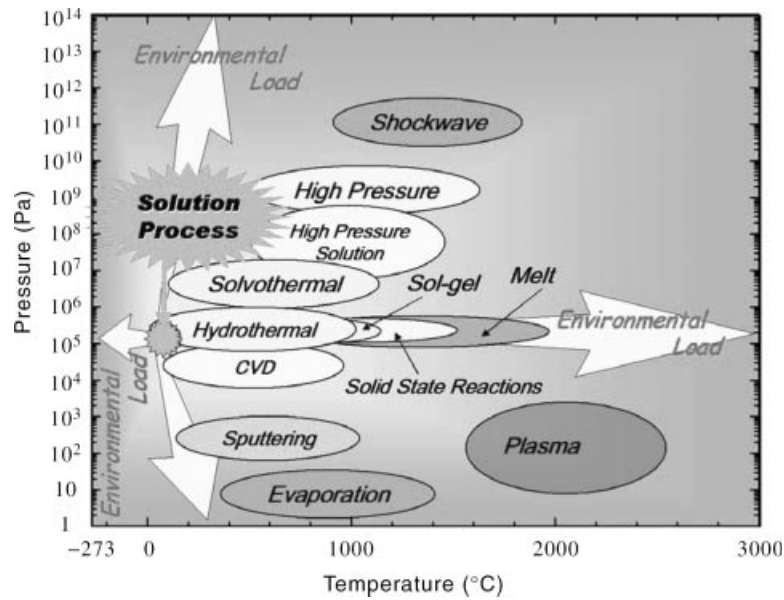
Fig. 1.   Pressure–temperature map of materials processing techniques (2).
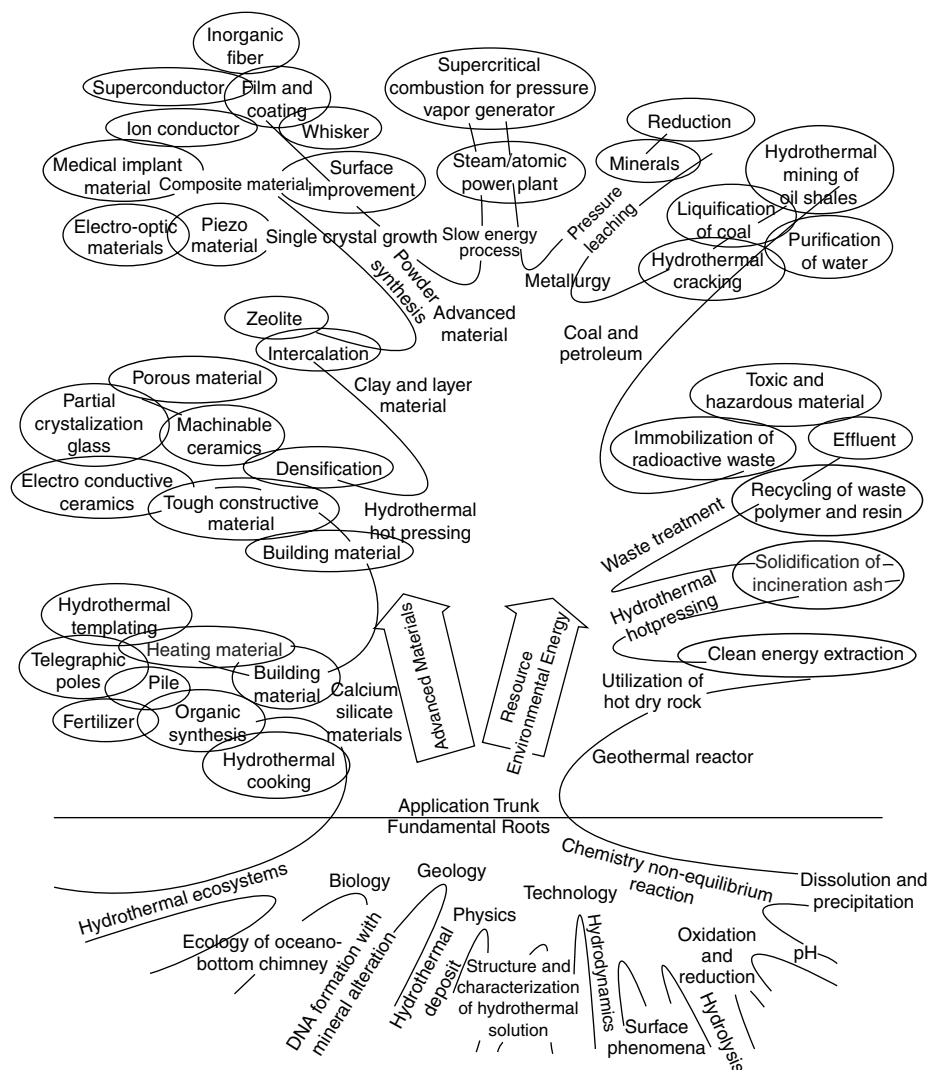
Fig. 2. Hydrothermal tree showing different branches of science and technology (1).
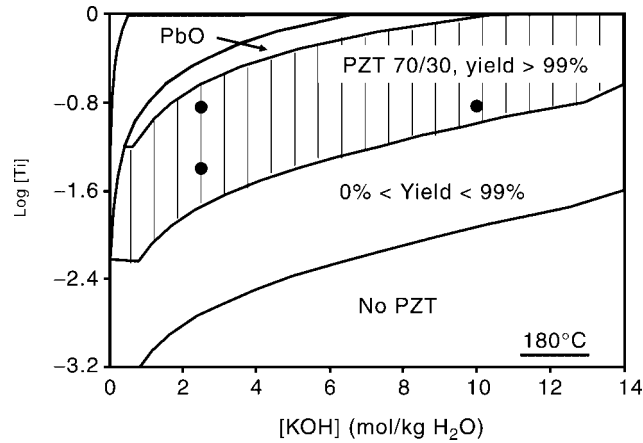
Fig. 3. Calculated stability field diagram for the PZT system at 180°C with KOH as the mineralizer (20).
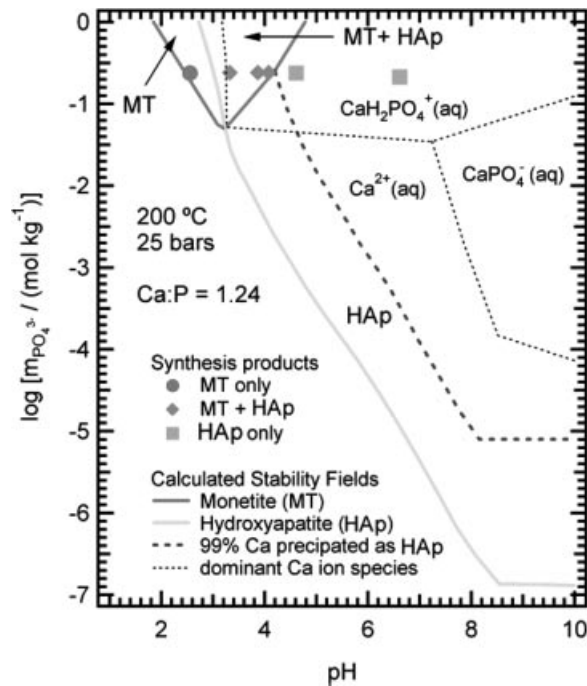

Fig. 4. The calculated stability field diagram for the HAp system at 200°C and 25 bars with a Ca/P ratio at 1.24. (K. Byrappa and R. E. Riman).

Fig. 5.   General purpose autoclave popularly used for hydrothermal treatment and hydrothermal synthesis.
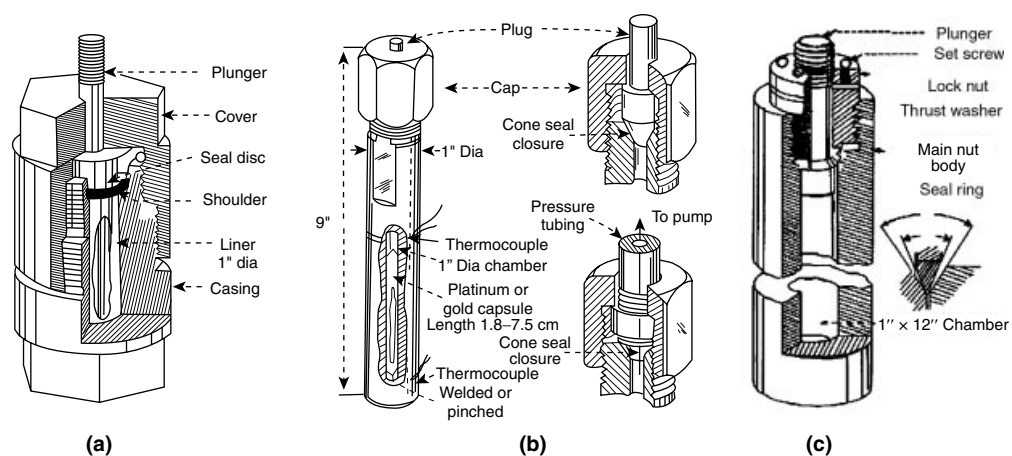
Fig. 6.   Commonly used autoclaves in hydrothermal processing of materials. (**a**) Morey autoclave. (**b**) Tuttle – Roy autoclave. (**c**) Modified Bridgman autoclave.
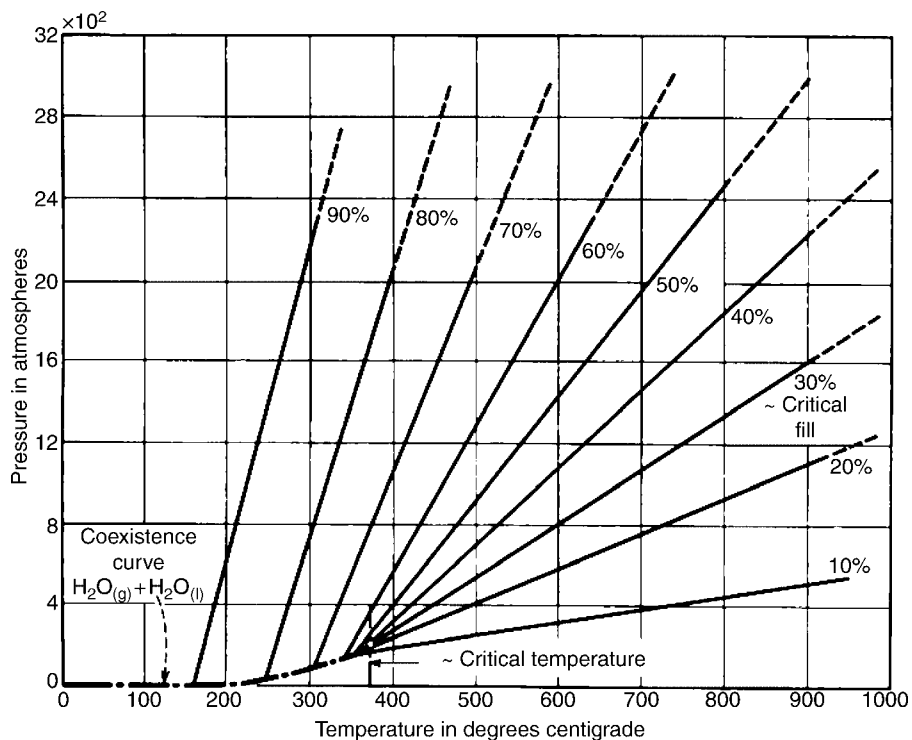
Fig. 7. Kennedy's PVT diagram for the SiO_2–H_2O system (23).

Fig. 8. Commercially available stirred reactors with facilities to withdraw the fluids and externally pump the desired gas into the autoclave, coupled magnetic stirrer assembly, and autoclave quenching facility with the circulation of chilled water through the cooling coils running inside the autoclave.
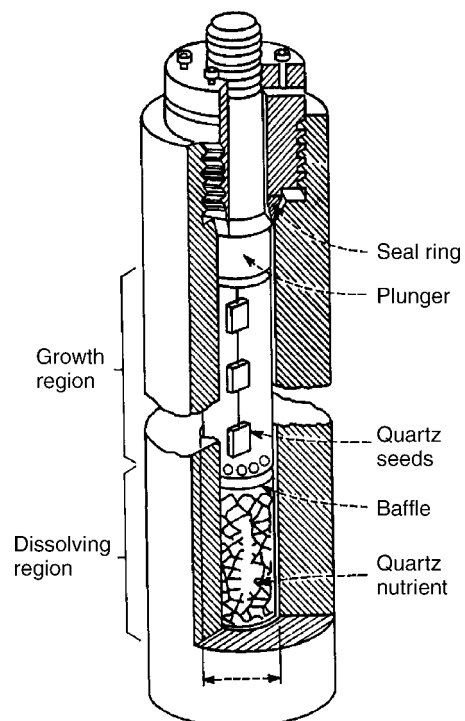
Fig. 9. Hydrothermal growth of quartz crystals using modified Bridgman autoclave (25).

Fig. 10. Quartz crystals from the world's largest autoclave at Toyo Communications Ltd., Japan. (Photo courtesy Prof. S. Taki.)
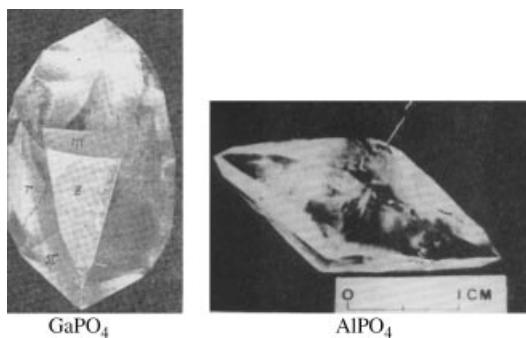
GaPO$_4$ AlPO$_4$

Fig. 11. Hydrothermally prepared GaPO$_4$ and AlPO$_4$ crystals. (Photo: Courtesy Prof. L. N. Demianets and Prof. Y. Toudic.)
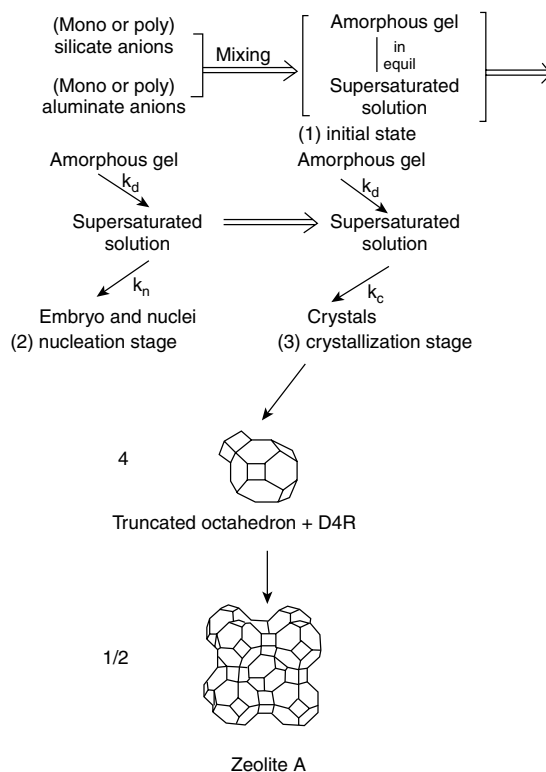
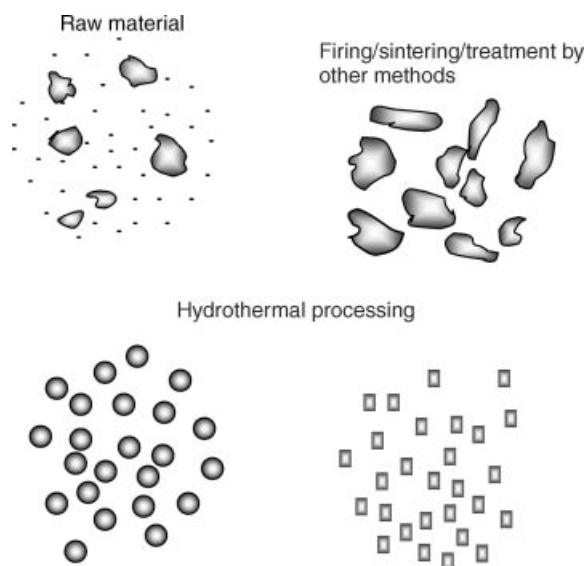**Fig. 12.**   Conceptual diagram of hydrothermal nucleation and crystallization of zeolite A (33).

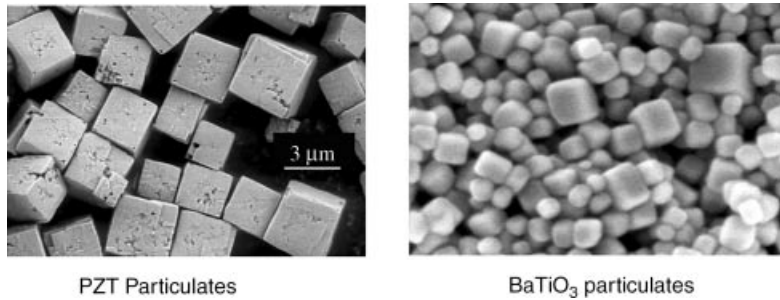**Fig. 13.**   Difference in particle processing by hydrothermal and convential ball-milling techniques.

PZT Particulates   BaTiO₃ particulates

Fig. 14. Hydrothermally prepared PZT and BaTiO$_3$ (50−200 nm) designer particulates with a controlled size and morphology. (Courtesy Prof. R. E. Riman.)
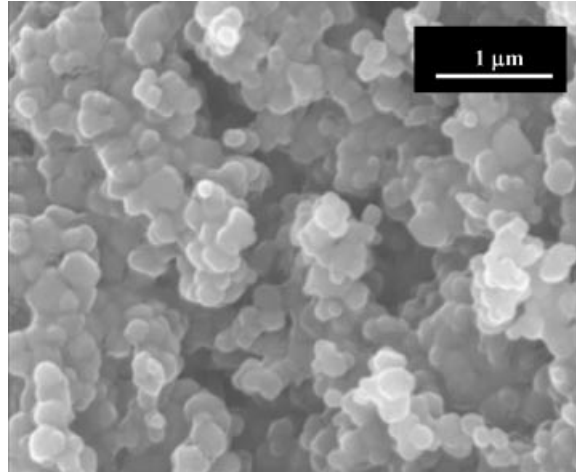

Fig. 15. Hydrothermally prepared TiO$_2$ powder particulates. (Photo from unpublished work of Prof. K. Byrappa.)
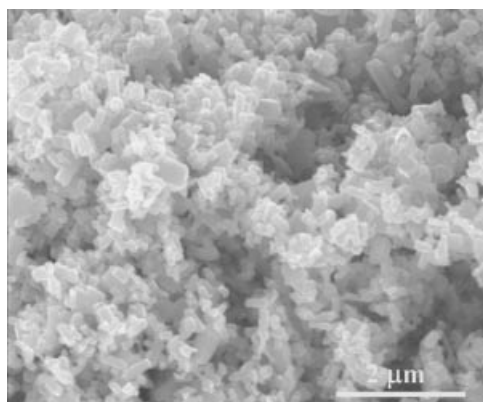
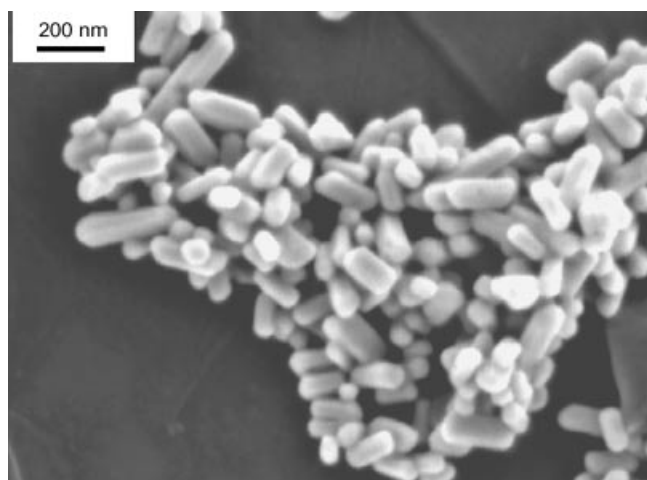**Fig. 16.** Hydrothermally prepared ZnO powder particulates. (Photo from unpublished work of Prof. K. Byrappa.)

Fig. 17. Hydrothermally prepared hydroxyapatite bioceramic particles. [Photo: K. Byrappa, R.E. Riman and W. Suchanek]
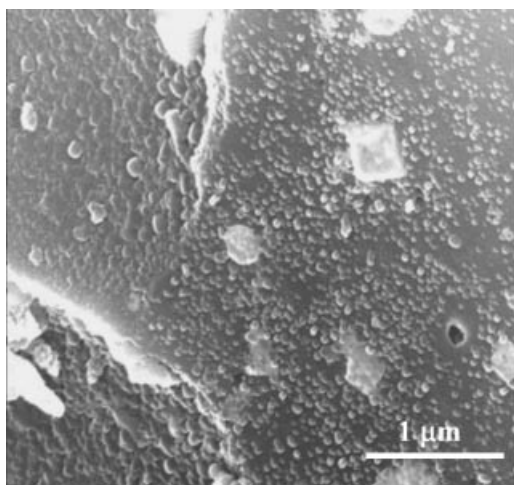
Fig. 18. Hydrothermally impregnated TiO_2:AC composite particulates. (Photo: K. Byrappa.)
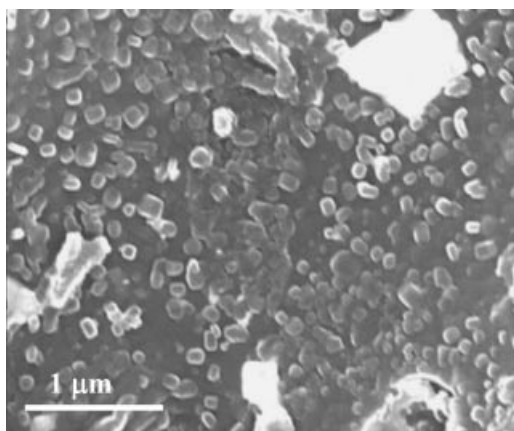

Fig. 19. Hydrothermally impregnated ZnO:AC composite particulates. (Photo: K. Byrappa.)

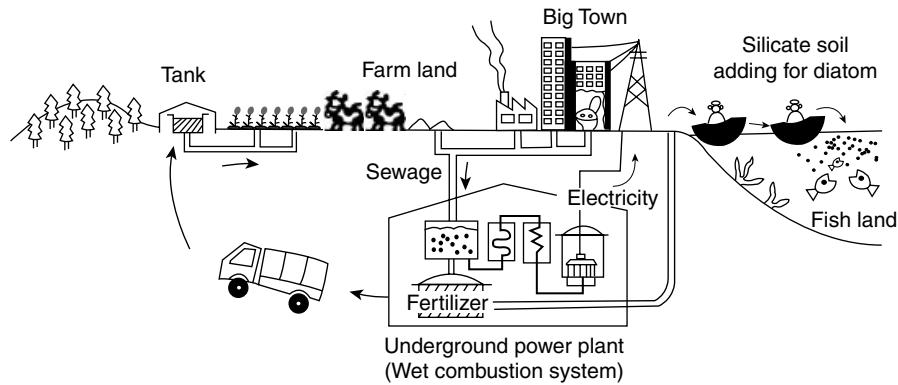**Fig. 20.** Author's imagination: a new generation complex industry constructed underground which exhaust no toxic or hazardous waste (54).
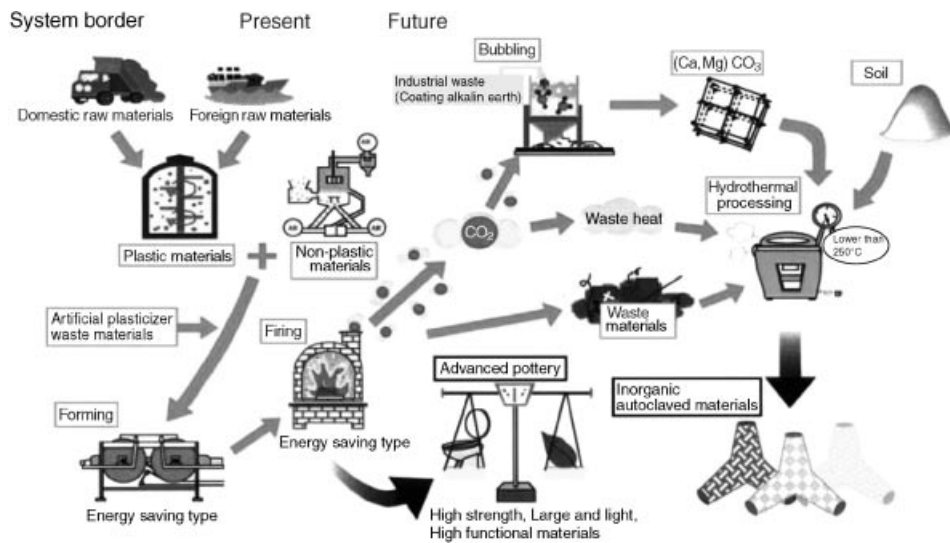

Fig. 21. Closed manufacturing system. (Courtesy of E. H. Ishida, Japan.)

Table 1. **Action of Hydrothermal Fluid (High Temperature−High Pressure Aqueous Solution / Vapor) on Solid-State Materials**

Classified	Action	Application
transfer medium	transfer of kinetic energy, heat, and pressure	erosion, machining abrasion, HIP forming, etc
adsorbate	adsorption−desorption at the surface	dispersion, surface diffusion, catalyst, crystallization, sintering, ion exchange, etc
solvent	dissolution−precipitation	synthesis, growth, purification, extraction, modification, degradation, etching, corrosion, etc
reactant	reaction	formation−decomposition (hydrates, hydroxides, oxides), corrosion, etc

Table 2. **Development of Hydrothermal Processing**

crystal synthesis and growth	oxide, sulfide, fluoride, ... (1978–)
controlled fine crystals composition, size, shape	PZT, ZrO_2, $BaTiO_3$, HAp, ferrite (1978–)
crystallized thin/thick films	$BaTiO_3$, $SrTiO_3$, $LiNbO_3$ (1989–)
etching, corrosion	oxide, nitride, carbide
polishing, machining	oxide, nitride, carbide
combined with electrical, photo-, radio-, and mechano-processing	synthesis, modification, coating
organic and biomaterials	hydrolysis, extraction
non-aqueous solution	polymerization, synthesis
continuous system	decomposition, wet combustion

Table 3. **Examples of Thermodynamic Calculations**

Species name	Inflows mol	Outflows	
		Liquid/mol	Solid/mol
H_2O	55.51	55.51	
$Ca(OH)_2$	0.1	7.2×10^{-6}	
CaO			
Ca^{2+}		1.5×10^{-2}	8.10×10^{-2}
$Ca(OH)^+$		4.0×10^{-3}	
H^+		4.45×10^{-13}	
OH^-		3.41×10^{-2}	
Total	*55.61*	*55.56*	*8.10×10^{-2}*

Table 4. **Commonly Used Autoclaves**

Type	Characteristic data
Pyrex tube 5-mm i.d., 2-mm wall thickness	6 bar at 250°C
quartz tube 5-mm i.d., 2-mm wall thickness	6 bar at 300°C
flat plate seal, Morey type	400 bar at 400°C
welded Walker-Buehler closure 2600 bar at 350°C	2000 bar at 480°C
delta ring, unsupported area	2300 bar at 400°C
modified Bridgman, unsupported area	3700 bar at 500°C
full Bridgman, unsupported area	3700 bar at 750°C
cold-cone seal, Tuttle-Roy type	5000 bar at 750°C
piston cylinder	40 kbar, 1000°C
belt apparatus	100 kbar, > 1500°C
opposed anvil	200 kbar, > 1500°C
opposed diamond anvil	up to 500 kbar, > 2000°C

Table 5. **Materials Used as Reactor Linings**

Material	$T\,°C$	Solutions	Remarks
titanium	550	chlorides	corrosion in NaOH solution > 25% in NH_4Cl solution > 10% (at 400°C)
		hydroxides sulfates sulfides	
armco iron	450	hydroxides	gradual oxidation producing magnetite
silver	600	hydroxides	gradual recrystallization and emrittlement, partial
dissolution			
platinum	700	hydroxides	blackening in chlorides in the presence of sulfur
		chlorides	ions; partial dissolution in hydroxides
		sulfates	
Teflon	300	chlorides hydroxides	poor thermal conduction
tantalum	500	chlorides	begin to corrode in NH_4Cl solution 78%
pyrex	300	chlorides	
copper	450	hydroxides	corrosion reduced in the presence of fluoride ions and organic compounds
graphite	450	sulfates	pyrolytic graphite most suitable for linings
nickel	300	hydroxides	
quartz	300	chlorides	
gold	700	hydroxides sulfates	partial dissolution in hydroxides

Table 6. **Comparison of Some Piezoelectric Characteristics**

Parameter	Quartz	AlPO$_4$ (Berlinite)	GaPO$_4$Gallium phosphate
coupling coefficient, $K\%$[a] $K\%$	8.5	11.0	>16.0
Q[a]	3×10^6	10^6	>5×10^4
α-β transition, $^\circ$C	573	584	no

[a] For AT cut.

Table 7. **Current Trends in the Hydrothermal Growth of Crystals**

Compound	Earlier work	Author[a]
$Li_2B_4O_7$	$T = 500–700°C$	$T = 240°C$
	$P = 500–1500$ bars	$P = {<}100$ bars
$Li_3B_5O_8(OH)_2$	$T = 450°C$	$T = 240°C$
	$P = 1000$ bars	$P = 80$ bars
$NaR(WO_4)_2$	$T = 700–900°C$	$T = 200°C$
R = La,Ce,Nd	$P = 2000–3000$ bars	$P = {<}100$ bars
R:MVO$_4$	melting point	$T = 100°C$
R = Nd,Eu,Tm;M = Y,Gd	$>1800°C$	$P = {<}30$ bars

[a] From the work of Prof. K. Byrappa.