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Hydrothermal processing of materials: past, present and future

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Abstract The hydrothermal technique provides an excellent possibility for processing of advanced materials whether it is bulk single crystals, or fine particles, or nanoparticles. The advantages of hydrothermal technology have been discussed in comparison with the conventional methods of materials processing. The current trends in hydrothermal materials processing has been described in relation to the concept of soft solution processing, as a single-step low energy consuming fabrication technique. Also some recent developments in multi-energy processing of materials such as microwave-hydrothermal, mechano-chemical-hydrothermal, electrochemical-hydrothermal, sonar-hydrothermal, etc. have been discussed. An overview of the past, present and future perspective of hydrothermal technology as a tool to fabricate advanced materials has been given with appropriate examples.

Introduction

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. It is well known that the largest single crystal formed in nature (beryl crystal of >1,000 kg) and some of the largest quantity of single crystals created by man in one experimental run (quartz crystals of several 1,000s kg) are both of hydrothermal origin [1]. Hydrothermal processing can be defined as any homogeneous (nanoparticles) or heterogeneous (bulk materials) 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 homogeneous or heterogeneous chemical reaction in the presence of a solvent *(whether aqueous or non-aqueous) above the room temperature and at pressure greater than 1 atm in a closed system* [2]. 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 conditions.* Similarly there are several other terms like *glycothermal, alcothermal, ammonothermal, carbonothermal, lyothermal*, and so on. Further, there is another school, which deals with the supercritical conditions for materials processing. The supercritical solvents (water or carbon dioxide) are popularly used to carry out a wide range of chemical reactions replacing organic solvents in a number of chemical processes, including nanoparticle fabrication, extraction, chemical manufacturing, waste treatment, recycling, etc. Many researchers call this a green processing or green chemistry. Here the authors use only the term hydrothermal throughout the text to describe all the chemical reactions taking place in a closed system in the presence of a solvent, whether it is aqueous or non-aqueous, whether it is

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sub-critical or supercritical. It means the roots of all these diversified processes like solvothermal, ammonothermal, glycothermal or supercritical fluid technology, etc., are hydrothermal technology only. Thus they are very closely related to one another except the solvent and the operating PT conditions. In this article the authors would review an overall progress in the area of hydrothermal processing of advanced materials covering all the above said set of processes along with the future perspective. The advanced material is referred to a chemical substance whether organic or inorganic or mixed (hybrid) in composition possessing desired physical and chemical properties. An overview of such advanced materials processing is the main focal point of this review.

There are several methods of processing advanced materials like physical vapour deposition, colloidal chemistry approach, mechanical milling, mechanical alloying techniques, sol–gel, mechanical grinding, hydrothermal, biomimitic, flame pyrolysis, laser ablation, ultrasound techniques, electrodeposition process, plasma synthesis techniques, microwave techniques, other precipitation processes, etc. Among these processes, the hydrothermal technique contributes to only around 6%. However, it has been realized that the hydrothermal technique facilitates the fabrication of even the toughest or the most complex material(s) with a desired physico-chemical properties. It has several advantages over the other conventional processes like energy saving, simplicity, cost effectiveness, better nucleation control, pollution free (since the reaction is carried out in a closed system), higher dispersion, higher rate of reaction, better shape control, and lower temperature of operation in the presence of an appropriate solvent, etc. The hydrothermal technique has a lot of other advantages like it accelerates interactions between solid and fluid species, phase pure and homogeneous materials can be achieved, reaction kinetics can be enhanced, the hydrothermal fluids offer higher diffusivity, lower viscosity, facilitate mass transport and higher dissolving power. Most important is that the chemical environment can be suitably tailored. Although the process involves slightly a longer reaction time compared to the vapour deposition processes, or milling, it provides highly crystalline particles with a better control over its size and shape. In recent years, much attention is being paid on the hydrothermal solution chemistry through thermodynamic calculations, which facilitate the selection of a proper solvent and appropriate pressure—temperature range, which not only help in synthesizing the products, but also to control the size and shape with a significant reduction in the experimental duration. A great variety of materials like native elements, metal oxides, hydroxides, silicates, carbonates, phosphates, sulphides, tellurides, nitrides, selenides, etc., both as particles and nanostructures like nanotubes, nanowires, nanorods, and so on have been obtained using the hydrothermal method. The method is also popular for the synthesis of a variety of forms of carbon like sp^2, sp^3 and intermediate types.

History of hydrothermal technology

The evolution of hydrothermal research is discussed here briefly. E.T. Schafthual was the first one to use hydrothermal method to prepare fine particles of quartz in a papin's digester during 1845 [3]. Followed by this, the synthesis of various silicates, clays, hydroxides and oxides minerals began. By 1900 more than 150 mineral species were synthesized including diamond [4]. Commercial application of the hydrothermal technique began in 1908 when K.J. Bayer leached bauxite mineral under hydrothermal conditions to obtain aluminium [5]. This opened up a new avenue for hydrothermal research in the area of metallurgy. Then followed the synthesis of various minerals, and during 1940s bulk crystal growth, phase equilibria studies, etc. S. Somiya has given the early stage of hydrothermal research, particularly in Japan in [11]. During 1970s and 1980s the multi-energy hydrothermal research nucleated in Japan and USA. Table 1 shows the evolutionary trend in hydrothermal processing of materials. Today hydrothermal method is popularly used in the processing of a wide range of materials not only the bulk crystals, but particles from fine to nanoparticles with a controlled size and morphology. There are lots of advantages with hydrothermal method when compared to the conventional methods of materials processing.

Current trends in hydrothermal technology

There is a great difference between the hydrothermal research carried out during the previous century and the early 21st century. During mid-20th century hydrothermal technology, which was in its peak was mainly focusing on the high temperature and pressure regime of materials processing, because of the lack of knowledge on the solubility of several compounds, and also on the selection of an appropriate solvent. The First International Hydrothermal Symposium (1982) held at the Tokyo Institute of Technology brought together specialists from interdisciplinary branches of science [15]. Since then the knowledge on the physical chemistry, PVT relationship in the hydrothermal systems greatly improved, which helped in drastically reducing the temperature and pressure conditions of processing. Similarly the solvothermal and supercritical processing which used a variety of other solvents like organic, organometallic complexes in materials processing,

Table 1 Development of hydrothermal processing of materials

Area	Period	Example, materials applied
1. Hydrometallulrgy	1900	Sulphate ore, oxide ore
2. Crystal synthesis, growth	1940	Quartz, oxides, sulphides fluorides, layered compounds
3. Fire crystals with controlled composition, size and shape	1970	PZT, ZrO_2, PSZ, $BaTiO_3$, hydroxyapatite
4. Whiskers	1980	Hydroxyapatite, Mg-sulphate, K-titanate
5. Crystalline films (thin, thick)	1980	$BaTiO_3$, $LiNbO_3$, ferrite, carbon, $LiNiO_2$
6. Hydrothermal etching	1980	Oxides, non-oxides
7. Hydrothermal machining	1980	Oxides, non-oxides
8. Combination with electro-, photo-, mechano-, electrochemical, etc.	1970–1980	Synthesis, alternation, coating, modification
9. Organic- or biomaterials	1980	Hydrolysis, wet-combustion, extraction, polymerization, decomposition, remediation
10. Solvothermal process	1980	Synthesis, extraction, reaction
11. Continuous process	1990	Synthesis, extraction, decomposition
12. Patterning	2000	Synthesis and fixing

thereby taking this technology towards Green Chemistry. Table 2 gives the trends in hydrothermal processing of materials, and take hydrothermal technology towards green technology for sustained human development since it consumes less energy, no or little solid waste/or waste liquid/gases, no recover treatment, no hazardous process materials, high selectivity, closed system of processing, etc. [6]. The important subjects of technology in the 21st 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 in the 21st century, viz., industrial ecology or the science of sustainability [7]. Hydrothermal chemistry has to be understood precisely in order to process the materials under soft and environmentally benign conditions. The behaviour of the solvent under hydrothermal conditions dealing with aspects like structure at critical, supercritical, and sub-critical conditions, dielectric constant, pH variation, viscosity, coefficient of expansion, density, etc. are to be understood with respect to pressure and temperature. Today much of the hydrothermal research is done based on the intelligent modelling of the hydrothermal reactions prior to the actual experiments. This greatly helps in predicting the experimental conditions to obtain a desired phase with a controlled shape and size [8, 9]. The modelling is based on the thermodynamic principles and today there are several commercially available softwares for thermodynamic calculations. One can precisely predict the experimental conditions and also construct the yield diagrams for a given system. Figure 1 shows the yield diagram for the hydroxyapatite system [10]. 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 and other systems.

Table 2 Current trends in hydrothermal technology [6]

Compound	Earlier work	Author[a]
$Li_2B_4O_7$	T = 500–700 °C	T = 240 °C
	P = 500–1,500 bars	P = <100 bars
$Li_3B_5O_8(OH)_2$	T = 450 °C	T = 240 °C
	P = 1,000 bars	P = 80 bars
$NaR(WO_4)_2$ R = La,Ce,Nd	T = 700–900 °C	T = 200 °C
	P = 2,000–3,000 bars	P = <100 bars
R:MVO_4 R = Nd,Eu,Tm;M = Y,Gd	Melting point	T = 100 °C
	>1,800 °C	P = <30 bars
$LaPO_4$	Synthesized at >1,200 °C	T < 120 °C
		P < 40 bars

[a] Byrappa K et al. [6]

New concepts in hydrothermal technology

More recently, the addition of external energy like microwave energy, sonar, or mechanochemical, electrical, magnetic, etc. into hydrothermal has opened up a new chapter in materials processing. It is being popularly referred to as multi-energy processing of materials. Because, hitherto in the hydrothermal technique the researchers were dealing only with the temperature, pressure and chemical potential as the three main variables in materials processing, and much of the thermodynamic issues have been understood more or less precisely. But with the additional energy variables in the system, the

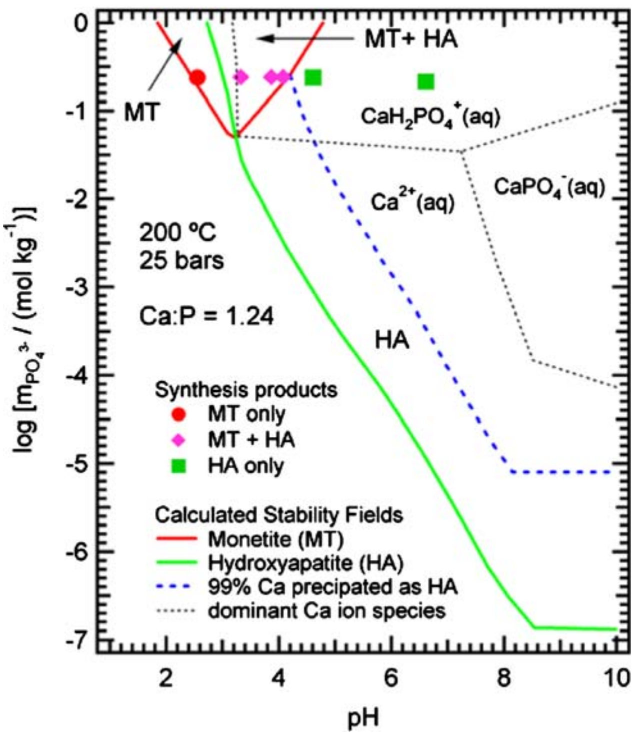


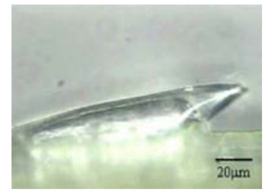
Fig. 1 Calculated stability field diagram for the HAp system at 200 °C and 25 bars with Ca:P ratio at 1.24 [10]

thermodynamic relationship reads completely different and most complicated. This forms the future of materials processing, which can be termed as novel methods of advanced materials processing [11, 12]. In the last 1 year, researchers are using the concept of instant hydrothermal reactions to obtain the desired nanoparticles in a shortest possible time and some even imagining a system like vending machine to produce the desired nanoparticles with definite physical properties [13]. This leads us to the concept visualized by an eminent American Energy Dept. consultant that *chemistry at the speed of light* [14]. There are so many advantages in such a multi-energy concept of advanced materials processing. The credit for this multi-energy processing goes to the researchers at the Tokyo Institute of Technology, who first attempted hydrothermal reactions with electrochemical and mechanical energy, which firmly established a new trend in materials processing in 1970s and 1980s [15]. Followed by this the Materials Research Laboratory at the Penn State, well explored the possibilities of microwave and sonar in the hydrothermal reactions in 1990s and went on to become the world leaders in this fascinating area of science [16, 17].

The discovery of hydrothermal activity in the deep sea during 1970s [18] has led to a new thinking in marine biology and geochemistry, which set a new trend in advanced materials processing. Now it is strongly believed that the roots of life on earth can be found in hydrothermal ecosystems. Thus the organic synthesis under hydrothermal conditions was established, which has now become an important area of research. The organic–inorganic hybrid materials are forming the core of the nanotechnology, which insist on the precise control over the size and morphology of the nanoparticles that influence directly the physical properties because of size quantization [19]. As we know, 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 vapour and heat (either external or internal). Water has a very important role in the formation of material or transformation of materials in nature, and hydrothermal circulation has always been assisted by bacteria, photochemical, and other related activities. Table 3 gives the bioassisted materials [20]. Such an understanding helps in the processing of advanced inorganic materials with the assistance of biomolecules, for example, proteins, organic ligands, DNA, amino acids, etc. A great variety of biomaterials can be fabricated under ambient conditions by employing the nature inspired conditions. M. Yoshimura is popularizing a new concept called *Soft Solution Processing*, for the past one decade, as the process which is inspired basically by the natural processes. It covers all set of materials processes, which can be operated under ambient or near ambient or just above the ambient conditions to prepare a wide range of materials including even complex and high melting materials [21–23]. The basis of the soft solution processing concept of Yoshimura is based on the nature inspired processes and the energy required in such processing. Figure 2 shows the energy versus performance/variety in bioprocess and artificial process. Soft processing is located as the third area between bioprocessing and the artificial processing. The bioprocessing can produce very useful materials in low energetic ways but for only limited species, size, shape and location. Whereas, the artificial processing can produce almost all materials, but it consumes high energy. Soft process targets the production of high performance materials by environmentally benign ways.

The features involved in the in situ fabrication of materials by soft solution processing covers direct or single-step formation of shaped/sized/deposited/oriented particles or ceramics with a minimized consumption of energy and resulting in any desired shape and size. Since the system acts as a closed flow system, thus makes it easy for charging, separation, cycling and recycling. We can achieve high deposition rate, and the entire process is highly versatile. The processes falling into the category of soft solution processing can be seen in Fig. 3. It shows advanced materials processing involving a single-step versus multi-step processes [23]. The in situ fabrication of the materials is the present trend in materials processing

Table 3 Bioprocessed materials (after S. Mann [20] and modified by M. Yoshimura)

Metallurgical materials	None (except for Au peromicrobium)		
Organic materials	Plenty and versatile		
Inorganic materials evolutionally	Limited and selected		Silica blade of Pampas grass
1. Silica (Opal)	Diatoms, Radiolaria	Skeleton	
	Plants	Leaves, Cell wall	
2. Iron oxides	Bacteria, Tuna, Salmon	Sensors	
	Chitons, Limpets	Teeth	
	Beaver, Rat, Fish	Teeth surface	
3. Iron sulphides	Gastropod	Dermal sclerite	
4. Ca carbonates	Mollusks, Gastropod	Shells	
	Corals	Cell wall	Gastropod with iron sulphide armor
	Cocolithophoridae	Cell wall scales	
	Aves	Egg shells	
5. Ca phosphates	Fish	Scales	
	Vertebrates	Bones	
	Mammals	Teeth	
	Chitons	Teeth	
6. Ca sulphate	Jellyfish	Gravity receptor	
Ba sulphates	Loxodes, Xenophyophora	Gravity receptor	
Sr sulphates	Acantharea	Skeleton	

Other Minerals (<100) are formed outside the bodies by bacterial process

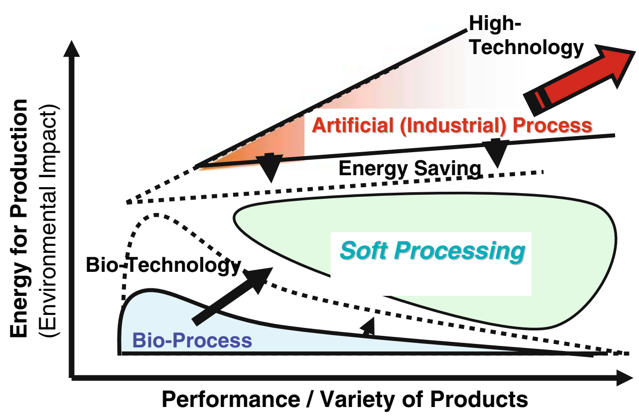


Fig. 2 Energy versus performance/variety in bioprocess and artificial process. Soft process targets the production of high performance materials by environmentally benign ways

without involving post-synthesis treatment. This is the greatest advantage of hydrothermal processing, which facilitates the in situ size, morphology control, and also surface modification. There are so many examples for such a processing approach, which will be discussed in detail later in this review. The hydrothermal processing is one of the most important techniques in soft solution processing. This special edition of the journal would cover most of the recent developments in hydrothermal technology. The authors here summarize the development in hydrothermal technology with an emphasis on its future perspective.

In solution processing the key parameter is the solvent. In case of hydrothermal processing the solvent plays multiple roles and its role has to be understood clearly in order to work out a mechanism for materials processing under hydrothermal conditions. Figure 4 shows the actions of hydrothermal fluids on the solid substances from physical action as the P,T medium to chemical action as the reactant. Accordingly we can expect the solvent to work as a medium providing the suitable environment, also it can act as an absorbent, as a solvent and reactant. Each action has a specific role to play in the hydrothermal reactions. Depending upon the action, the application and the apparatus are selected for hydrothermal processing of materials.

Apparatus in hydrothermal research

In recent years, there is not much of focus on the designing of new instrumentation for conventional hydrothermal processing of materials. We can divide this aspect into two areas. The first one deals with the geological and geophysical studies, where extreme and pressure reactors, belt apparatus, piston cylinder and anvil type apparatus are popularly used. The second area deals with the materials

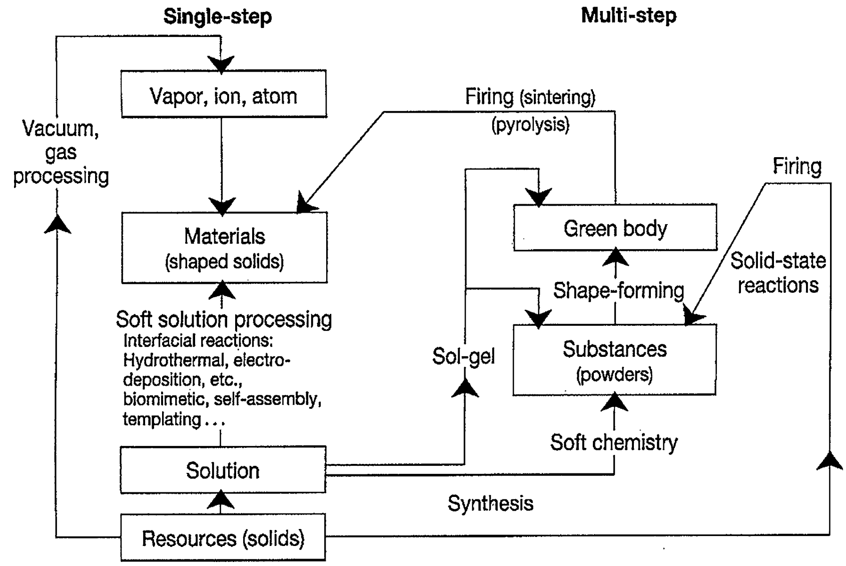


Fig. 3 Schematic diagram of advanced-materials processing showing single-step versus multi-step processes [23]

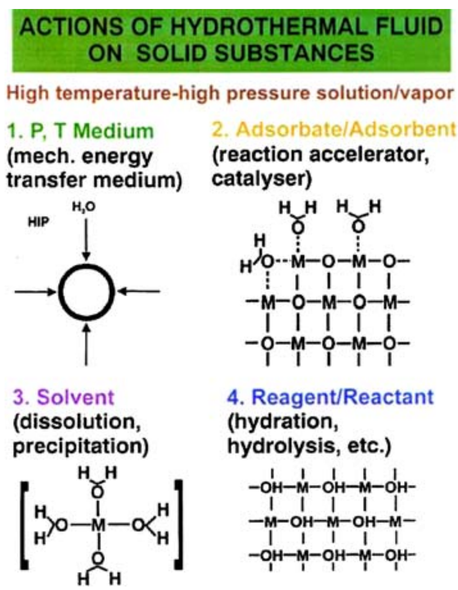


Fig. 4 Action of hydrothermal fluid on solid substances

processing in industries and academia, wherein the pressure and temperature conditions of processing are becoming more and more environmentally benign through operations under milder conditions. Here, most of the researchers and industrialists/commercial manufacturers of materials use large volume simple design reactors, flow-cells, the Tuttle type batch reactors for higher temperature and pressure operations for academic interest, General purpose autoclaves, stirred reactors, etc. Compared to the first half of the 20th century this area is not being studied actively. However, the designing and fabrication of apparatus related to the hydrothermal technique with multi-energy applications like hydrothermal with microwave, or sonar, or mechanical, magnetic, and also for the waste-free processing of materials, is still an attractive area of research.

Hydrothermal processing of selected functional materials

In this special edition of the journal, a wide range of materials and issues related to hydrothermal technology have been covered by the editors, and hence, the authors here discuss only the most important materials in order to show the trend in hydrothermal research with a future perspective. The materials processing has been discussed here keeping in mind the past, present and future with respect to the crystal growth, fine particles, nanomaterials and composites.

Hydrothermal crystal growth

The focus of hydrothermal technology in the earlier days was exclusively on the growth of bulk single crystals. The earliest materials to be grown was quartz followed by a wide range of mineral species in the bulk form like ruby, corundum, and a lot of other silicates, carbonates, phosphates, sulphates, etc. However, the success of hydrothermal technology was limited to the growth of quartz crystals. Over 5,000 kg of quartz is produced in one experimental run in a single large autoclave. So far no other crystal could match the size and quantity of quartz produced in a single experimental run using the hydrothermal technique. Today much of the commercial production of bulk single crystals using hydrothermal technology is still restricted to quartz, coloured quartz, emerald, corundum, ruby, etc. Hence, from1970s onwards the use of hydrothermal technology for the growth of other large single crystals declined significantly. In the recent years there is again a growing interest in the use of hydrothermal technology for the single crystal growth of ZnO, $GaPO_4$, GaN, and Langesite. All the four crystals are regarded as the strategic materials owing to their exceptional properties. We can discuss here briefly the growth of these four materials.

Hydrothermal growth of ZnO

Zinc Oxide is a promising material of photonics because of its wide bandgap of 3.37 eV and high exciton binding energy of 60 meV. The wide bandgap makes ZnO a suitable material for short wavelength photonic applications while the high exciton binding energy allows efficient exciton recombination at room temperature. It is used as varistors, transparent high power electronics, optical waveguides, piezoelectric converters, gas-sensing analyzers, window materials for display and solar cells, etc. In the recent years, ZnO bulk crystals are used as the substrate materials for the epitaxial growth of GaN. Using the hydrothermal technique, ZnO is being processed as bulk single crystals, fine particles, thin films, and nanoparticles.

In case of single crystal growth of ZnO, highly alkaline solutions are used as solvents and usually (0001) and (1010) seed plates are used for the bulk crystal growth. The experimental temperature in the dissolution zone in the range of 350–360 °C and pressure in the range of 20–40 MPa have been used. The largest single crystal of ZnO obtained so far by researchers is around 180–200 g and the experimental duration is still very high [24–26]. The precise solubility data and the ideal solvent for ZnO growth are still far from reality to achieve the bulk single crystal growth on par with that of quartz. However, there are many groups all over the world working on the growth of ZnO bulk crystals [27–29]. There are several articles in this issue devoted to the synthesis of ZnO both as bulk crystals, thin films and nanoparticles [30–33].

Hydrothermal growth of $GaPO_4$

Gallium phosphate is known as isoelectronic and isostructural with alpha-quartz. In fact gallium phosphate has better piezoelectric properties than that of alpha-quartz [34]. Also it has no phase transitions unlike quartz. Hence, it is highly suitable for high temperature electronic applications. However, owing to its solubility issues, the success in the growth of large size crystals of gallium phosphate has not been achieved so far in spite of its growth began more than two decades ago. There are many groups in Russia and France working on the growth of this crystal for electronic industries. The largest size of the gallium phosphate crystal grown is around 3 cm long. The growth experiments are carried out in the temperature range 170–240 °C and pressure 15–35 MPa, using the mixed acid mineralizers [35]. Despite the fact that the growth rate even as high as 0.5 mm/day has been achieved depending upon the type of solvent, the ionic strength of the solvent falls after a few days and the crystals do not grow further. If the ionic strength is stabilized by adding some sequestering agents externally whenever required, then the large size crystals can be grown. But the addition of sequestering agents during the growth externally would lead to formation of physical defects, which hampers its device potential.

Hydrothermal growth of GaN

Bulk crystal growth of gallium nitride is one of the fastest growing research interests among crystal growers. Gallium nitride is a wide band gap semiconductor, which is far superior to the classical semiconductors like Si or GaAs in some special device applications, especially for photonic and electronic devices. Gallium nitride laser diodes offer over a six-fold increase in storage capacity for the next generation of DVDs, while gallium nitride LED based illumination sources is 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 [36–40]. However, there is a major problem related to the production of high quality GaN crystals from the conventional techniques like the melt or physical vapour deposition techniques uneconomical and reliable because of the high volatility of gallium nitride. The solvothermal technique, particularly the ammonothermal method has been proved to be the most suitable technique for nitride synthesis. There are two articles in this special edition devoted to the synthesis of nitrides [41, 42].

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 the 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 temperature between 300 and 600 (C. GaN shows retrograde solubility and over 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 per day on 1-cm^2 seeds. Though numerous experiments have 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. But the bulk growth of defect free crystals of gallium nitride still needs a coherent research activity [43].

Hydrothermal growth of langasite

Langasite is one of the most popular piezoelectric crystals, which is drawing much attention from researchers for the past decade owing to its superior electronic properties compared to all other existing piezoelectric materials. Its mainly used for the intermediate frequency-surface acoustic wave filters which are employed in the base station of the third generation mobile communication system such as the wide band-code division multiple access. The most significant aspect of its application is that there exists a certain orientation along which the SAW propagates without any dispersion that enables the robust shape of the passband. Also langasite crystal is a high temperature or pressure sensor operating at high temperature up to 1,000 °C. It does not show any phase transition until it melts at around 1,500 °C. Further, the combustion sensor for automobile employs a langasite diaphragm and allows the most suitable mixing ratio of air and fuel, resulting in the superior energy conservation [44–46].

The growth of langasite is popularly carried out by melt methods, particularly Czochralski or Bridgman techniques [47–50]. However, the greatest problem with these melt grown crystals is the compositional homogeneity and the phase diagram for the system La_2O_3–Ga_2O_3–SiO_2 is so complicated, and one can expect a lot of additional phases as admixtures. Also the chemical zoning is seen in these melt grown crystals. Therefore, in the last couple of years, researchers are looking into the possibilities of growing this crystal using the hydrothermal technique in order to control the stoichiometry and phase homogeneity. If the researchers succeed in growing this crystal using hydrothermal technique as bulk single crystals as big as several inches length, it will bring in a revolutionary changes in the hydrothermal technology for growing single crystals and it will replace the quartz in electronic industries. Since this crystal has no phase transition, it gives a great option for wide range of PT conditions of growth. As per the data gathered by the present authors through personal discussion with some of the active researchers working on langasite growth, the temperature employed is around 300–350 °C and melt grown langasite crystals are being used as seeds.

There are many more important bulk crystals being grown using hydrothermal technology like potassium titanyl phosphate, lithium tetraborate, lithium aluminate, etc. However, the multi-energy approach to enhance the growth kinetics in the bulk crystal growth has not been attempted, since it would induce more physical defects in the grown crystals.

Hydrothermal processing of fine particles

Processing of fine particles under hydrothermal conditions is known ever since hydrothermal technology was born. Majority of the early hydrothermal experiments carried out during 1840s to early 1900s mainly dealt with the fine to nanocrystalline products, which were discarded as failures due to the lack of sophisticated tools to examine the fine products except some chemical techniques [51]. During this period lots of experiments were carried out on the synthesis of fine particles of zeolites, clays, some silicates, hydroxides, etc. [52]. When Barrer reported the hydrothermal synthesis of fine particles of zeolites during 1940s, it opened a new branch of science, viz. molecular sieve technology. During late 1960s and 1970s, attempts were made to synthesize fine ceramic particles, especially metal oxides using hydrothermal method. It was a most popular field of research under hydrothermal [1, 53, 54]. A great variety of ceramic materials were synthesized, and the significance of the hydrothermal technique was realized in the processing of highly crystalline fine ceramic particles [55, 56]. This also showed the advantages of hydrothermal technique over other conventional techniques like firing, heat treatment, moulding, hot pressing, etc. The hydrothermal research during 1990s marks the beginning of the work on the processing of fine to ultra-fine particles with a controlled size and morphology. Today, it has evolved as one of the most efficient methods of soft chemistry in processing the advanced materials like fine to nanomaterials with a controlled size and shape. Table 4 shows the comparison of various powder processing methods [23]. As evident from Table 4, 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, and so on. Figure 5 shows the major differences in the products obtained by ball milling or sintering or firing and hydrothermal methods [6]. Currently, the annual market value of electronic ceramics is over a billion dollar, and the market for nanoparticles processing in 2002 was 120 billion dollars and now raising at the rate of 15% annually and reach 370 billion dollars by 2010, and as per NSF prediction it would jump into a trillion dollar industry by 2015.

Of all the ceramics, the PZT family of ceramics has been studied extensively using the hydrothermal technique.

Table 4 Comparison of various powder synthesis methods [23]

Parameter	Solid state reactions	Co-precipitation	Sol–Gel	Polymerizable complex	Hydrothermal
Cost	Low to moderate	Moderate	High	High	Moderate
State of development	Commercial	Demonstration/commercial	R & D	R & D	R & D/demonstration
Compositional control	Poor	Good	Excellent	Excellent	Good/excellent
Morphology control	Poor	Moderate	Moderate	Moderate	Good
Powder reactivity	Poor	Good	Good	Good	Good
Purity (%)	<99.5	>99.5	>99.9	>99.9	>99.5
Calcination step	Yes (multiple)	Yes	Yes	Yes	No
Milling step	Yes (multiple)	Yes	Yes	Yes	No

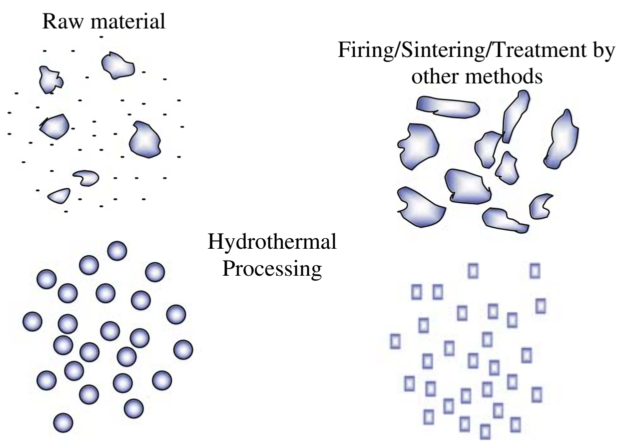


Fig. 5 Difference in particle processing by hydrothermal and conventional ball milling techniques [6]

From early 1980s several thousands of reports have appeared on the preparation of these ceramics. Thermodynamic calculation and kinetics of these systems have been studied extensively [8, 10]. Several new variants/approaches in the processing of these electronic ceramics have been reported to enhance the kinetics, to shorten the processing time, to control the size and shape, to maintain the homogeneity of the phases and to achieve reproducibility. A great variety of precursors and also the solvents have been attempted in the processing of these ceramics. Similarly fine film formation of these ceramics on an appropriate substrate has been accomplished by several workers [57, 58]. Here we would like to discuss only some selected works to show the trend in hydrothermal technology and to link it with the soft solution processing.

The most significant part of the processing of these ceramics during 1980s and 1990s was the introduction of multi-energy concept of materials processing keeping the hydrothermal technique as the basic one. In this respect the electro-chemical hydrothermal is one of the most important developments in advanced materials processing. This was popularized as mentioned earlier by the researchers of Tokyo Tech, Japan. The basic design of the hydrothermal electrochemical cell is shown in Fig. 6 [59]. Using this kind of apparatus a great variety of advanced ceramics have been fabricated with a precise control over their formation. Figure 7 shows the materials prepared using hydrothermal electro-chemical method [60–62]. The hydrothermal electro-chemically prepared specimen did not show any exfoliation even after bending. Besides, electronic ceramics, several other mixed oxides like spinel ferrites, titanates, tantalates, tungstates, vanadates, etc. and their composites have been processed as thin films crystallized on various substrates using this soft solution processing method (under mild hydrothermal conditions). These studies provided ample evidence during 1980s that the materials can be processed under soft hydrothermal

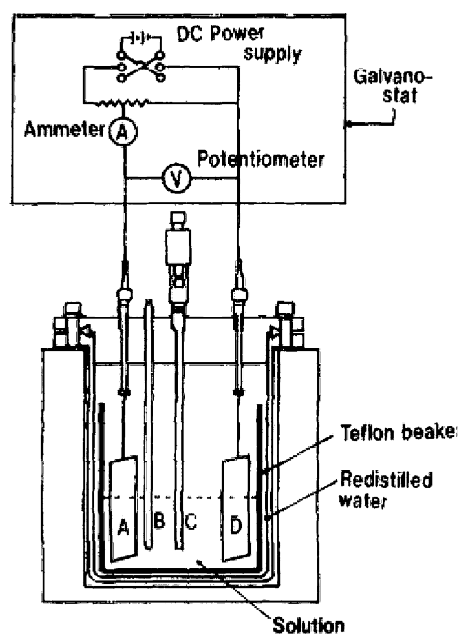


Fig. 6 Schematic illustration of experimental equipment for hydrothermal-electro-chemical method: (A) cathode (Pt plate); (B) thermocouple; (C) stirrer; (D) anode (Ti plate) [59]

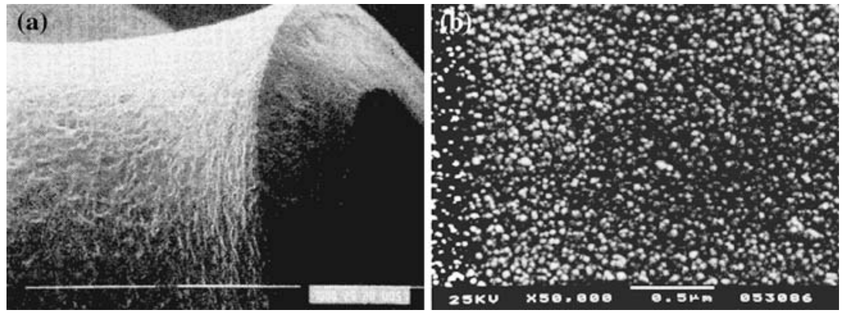


Fig. 7 Electronic ceramics prepared using hydrothermal electro-chemical method: (**a**) $BaTiO_3$ film on Ti substrate (T = 200 °C in 0.5 N $Ba(OH)_2$ solution with (**b**) 15 mA/cm^2 for 30 min; (**b**) $BaTiO_3$ film on Ti deposited polymer substrate at 150 °C in 3 N $Ba(OH)_2$ solution for 1 h [61, 62]

conditions in a short span of time using the multi-energy concept of materials processing. Followed by these studies, there was a surge in the activities related to the use of external energy like microwave energy, sonar, or mechanochemical, etc. into the hydrothermal technique giving distinct advantages over the conventional hydrothermal method in the rapid crystallization of a great variety of nanomaterials. Amongst these the microwave-hydrothermal technique has been studied extensively to prepare materials [63]. Using this microwave-hydrothermal method rapid crystallization of rutile, anatase, Ni, Zn, Co and Mn ferrites, barium titanate fine particles, etc. has been achieved [64, 65]. In the earlier days of such microwave-hydrothermal processing of materials, there was not much control over the products homogeneity and also the morphology and size. Also the products were highly agglomerated. Towards the end of the last century these issues were worked out in detail, and the microwave-hydrothermal not only became a tool for rapid processing of materials, but one could understand the mechanism of these processes to some extent, which helped to tune the process to obtain the target material in a desired shape and size. Figure 8 shows the direct fabrication of oxide films by microwave-hydrothermal method at low temperature [64]. This work shows that $BaTiO_3$ films could be directly fabricated on Ti substrates at low temperature (100 °C) and short holding time (below 1 h). Like wise, several researchers have reported the processing a variety of ceramics and other materials using hydrothermal with sonar, mechanochemical, and so on. The most prominent among them is the hydrothermal-mechanochemical reactions to synthesize fine particles of hydroxyapatite, titania, and also some hybrid materials [66, 67].

The important step in the processing of fine particles of advanced materials is the use of surfactants and chelates to control the nucleation of a desired phase, such that the phase homogeneity, size, shape and dispersibility could be achieved during the crystallization of these fine particles. This marked the beginning of the study of precursor preparation for different systems, the surface interactions with the capping agents or surfactants, and polymerized complexes. The surfaces of the particles could be altered to hydrophobic or hydrophilic depending upon the applications [30, 68]. Today this approach is playing a key role in nanotechnology to prepare highly dispersed, oriented and self-assembled particles. Figure 9 shows the new preparative chemical approach for the precursors preparation. Such an approach leads to the processing of highly controlled and also self-assembled particles of even complex and multi-component materials. Using such an approach a wide range of advanced materials like lead zirconium titanate (PZT) family of ceramics, ferrites, phosphates, sulphides, oxides, hydroxyapatites, etc., and composites have been prepared as fine particles for technological applications with preferred morphology such as whiskers, rods, needles, plates, spheres, etc. depending upon the applications. This precursor based chemical approach to hydrothermal synthesis has made a tremendous progress in recent years and also drastically reduced the temperature and pressure conditions of processing of materials taking it towards the soft solution processing, which not only includes hydrothermal, but all other wet chemical or solution approaches including biomimitic. Some of these processes have been accomplished under ambient conditions. Therefore, the soft solution processing and the soft chemistry routes are the future of materials processing.

Hydrothermal technology for nanotechnology

The nanomaterials are known for their unique mechanical, chemical, physical, thermal, electrical, optical, magnetic and also specific surface area properties, which in turn define them as nanostructures, nanoelectronics, nanophotonics, nanobiotechnology, nanoanalytics, etc. In the last one decade a large variety of nanomaterials and devices with new capabilities have been generated employing nanoparticles based on metals, metal oxides, ceramics (both oxide and non-oxide), silicates, organics, polymers, etc. One of the most important properties of materials in nanosize regime is the changing physical properties. Nanoparticles possess unique optical and electronic

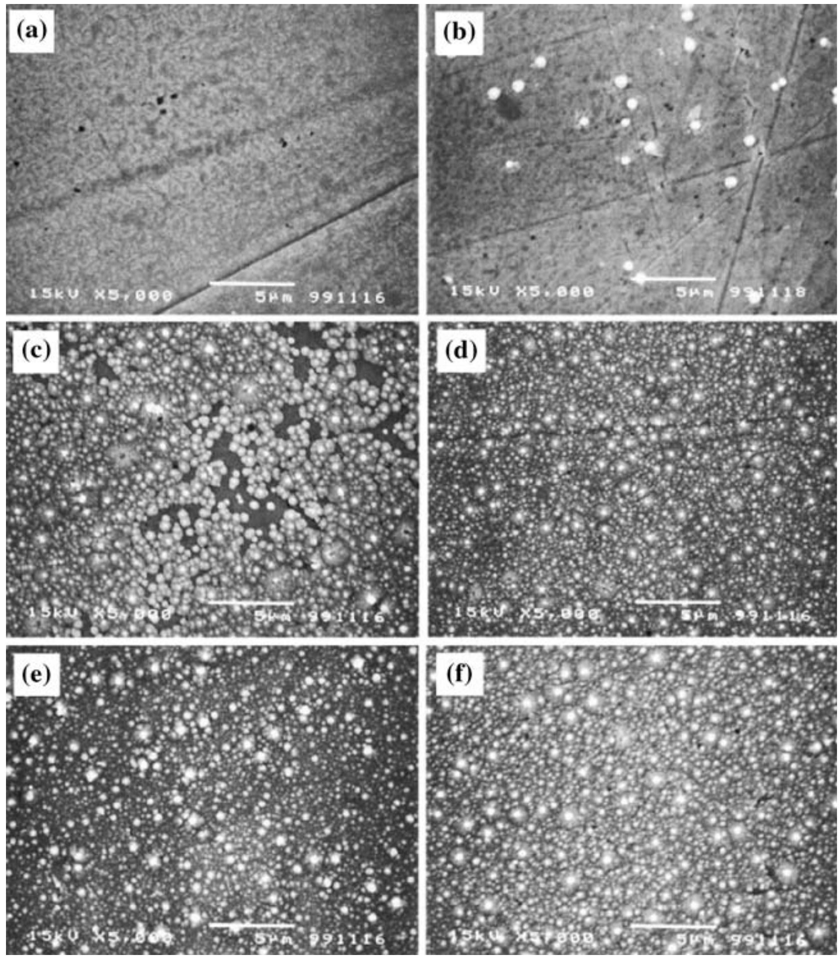


Fig. 8 SEM photos of the surface of $BaTiO_3$ films fabricated by the microwave-hydrothermal method at 100 °C: (**a**) Ti-metal; (**b**) 5 min; (**c**) 10 min; (**e**) 30 min; (**f**) 60 min [64]

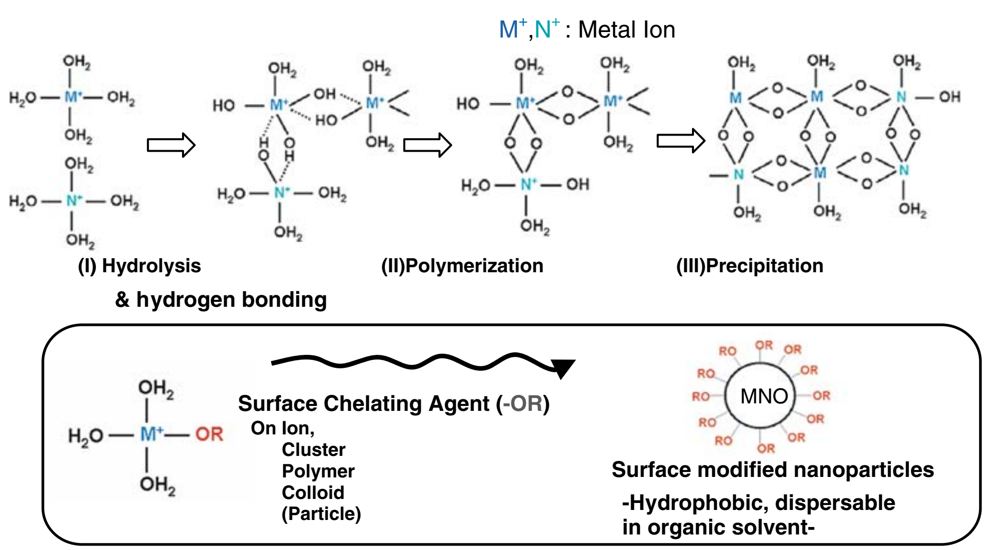


Fig. 9 Modifiers and chelating agents used in the preparation of fine particles

properties not observed for corresponding bulk samples. Owing to a substantial increase in the fraction of surface atoms and to increasing role of the surface effects not only the optical properties but also other characteristics of materials (structure of electronic energy levels and transitions, electron affinity, conductivity, phase transition temperature, magnetic properties, melting points, etc.) also become dependent on the nanoparticle size and shape. Such a size dependent properties have been exploited for biological tagging, for example, as fluorescent biological labels. Hence, it is extremely important to control the size and also shape of the nanoparticles/nanocrystals in order to obtain a desired physical property. Therefore, the field of functionalization is almost endless and represents an enormous space to explore. This in combination with molecular imaging can provide a new branch of science viz. nanobiotechnology imaging research. A major challenge in the nanomaterials science is the accurate control of the size and shape, which in turn is directly linked with the nanomaterials processing method. Nanoparticles can be obtained from a great variety of processes involving the conversion of solid to solid or liquid to solid or gas to solid. The stringent requirements for the biological applications like the therapeutic, bioimaging, hyperthermia, targeted drug delivery system, biosensors, MRI, microelectronics, etc. insist on the control of the size and shape of nanomaterials. Hence, the solution techniques like hydrothermal is becoming the most valuable nanomaterials fabrication tool in the recent years, and it has an edge over all other processing methods because of the high quality of products. By choosing the appropriate capping agents, surface properties of the nanoparticles can be significantly altered from hydrophilic to hydrophobic and vice versa. Also a perfect dispersion of the nanoparticles in the given solvent can be achieved for making the self-assembly structures. The knowledge on the nucleation, crystallization, self-assembly, and the growth mechanism of the nanocrystals in hydrothermal solution media are rather complicated and are still not well understood.

Gold nanoparticles have been around since Roman times. As per the literature data, Michael Faraday was the first to seriously experiment with gold nanoparticles starting in the 1850s [69]. The development of new sophisticated tools like STM, TEM, AFM, etc. to observe, measure and manipulate processes at the nanoscale level gave a breakthrough to the nanotechnology. Majority of the early hydrothermal experiments carried out during 1840s to early 1900s mainly dealt with the nanocrystalline products, which were discarded as failures due to the lack of sophisticated tools to examine the fine to nanoproducts except some chemical techniques [51, 70–72]. Until the works of Giorgio Spezia in 1900, the hydrothermal technology did not gain much importance in the growth of bulk crystals, as the products in majority of the cases were very fine grained and sub-microscopic in size without any X-ray data [73]. But today, it has evolved as one of the most efficient methods of soft chemistry in processing the advanced materials like nanomaterials with a controlled size, shape and physical characteristics.

A great variety of nanomaterials have been obtained using the hydrothermal method. Amongst them the native elements, metal oxides, hydroxides, silicates, carbonates, phosphates, sulphides, tellurides, nitrides, selenides, etc. both as particles and nanostructures like nanotubes, nanowires, nanorods, etc. The method has been popularly used for the synthesis of a variety of nanoforms of carbon like sp^2, sp^3 and intermediate types.

In hydrothermal synthesis the most popularly used reactors for the synthesis of nanoparticles are: General Purpose autoclaves, Morey autoclaves, Batch type reactors, Tuttle-Roy type reactors, etc. These reactors work in the pressure range from a few bars to several kilobars. Like in the case of fine particles preparation, the addition of external energy like microwave energy, electrochemical, sonar, or mechanochemical, etc. into the hydrothermal technique has distinct advantages over the conventional hydrothermal method in the rapid crystallization of a great variety of nanomaterials. Amongst these the microwave-hydrothermal technique has been studied extensively to prepare nanomaterials.

Rustum Roy, M. Yoshimura, Y.-T. Qian, G. Demazeau, and N. Yamasaki, have pioneered the low temperature soft hydrothermal processing technique for preparing highly oriented, dispersed, self-assembled nanoparticles with a great control over size and morphology, for a wide variety of compounds ranging from native metals, sulphides, selenides, metal oxides, hydroxides, ferrites, PZTs, carbonates, silicates, tantalates, titanates, vanadates, carbon polymorphs, etc [74–77]. Their approach is unique, and soft processing methods have been employed through an appropriate solvent and precursor selection. Also some of them have used the external energy like microwave, sonar, electro-chemical, mechanochemical, milling, magnetic, etc. with hydrothermal to prepare the some of the above said variety of nanomaterials. Similarly, T. Adschiri and K. Arai have pioneered the hydrothermal technique under supercritical conditions for processing a wide range of metal oxides, hydroxides, and so on. They have extensively studied the theoretical and experimental aspects of this technique and proposed a systematic mechanism of formation of various metal oxide nanoparticles under supercritical hydrothermal conditions [78, 79]. In recent years, Adschiri and group have extended this technique for a wide range of other materials like organic–inorganic hybrid materials with a perfect control over the particle formation, size, morphology and self-assembly [68, 80]. Since, the subject of nanomaterials processing under hydrothermal conditions is a vast one in the present day context, here the authors discuss only a selected group of nanomaterials processing to show the present trend and the future direction in hydrothermal processing of materials. Also the most recent trend in hydrothermal nanomaterials processing related to the direct formation of nano-particles for various oxides in a single-step soft processing methods without firing or the presence of highly oxidizing agents would be discussed.

Ceria based oxide nanoparticles are being studied extensively for a variety of applications like catalysis, ultraviolet adsorbers, gas sensors, abrasive, electrochemistry, optics and also biological applications [81]. Structural, optical, electronic and catalytic properties of ceria based oxide nanocrystals are strongly dependent on their crucial geometrical parameters like size and shape. Therefore, the preparation of high quality of ceria nanocrystals of desired morphology is of great fundamental and technological interest. There are several groups in the world working on the hydrothermal processing of ceria based oxide nanoparticles [81–83]. In order to obtain surface modification and a desired size and shape, several modifiers are being used by researchers. A variety of organic acids and amines are being used for this purpose. Figure 10a shows the TEM image of CeO_2 nanoparticles obtained through such an approach by Taniguchi et al. [84]. This figure shows the self-assembly of fine nanoparticles of several nanometers size. The valency state of the Ce ions alter with the size of the nanoparticles, and a control over such an alteration is quite important in nanomaterials processing. Similarly, Ahniyaz et al. [85] have obtained fine nanoparticles of 5 ± 1 nm size particles of ceria–zirconia solid solutions ($Zr_{0.5}Ce_{0.5}O_2$). A clear solution of 0.2 M $Ce(NO_3)_3$ and $ZrO(NO_3)_2$, was treated hydrothermally at 120 °C for 6 h in the higher pH region (>9.0). Figure 10b shows the TEM photos of ceria–zirconia solid solution nanoparticles [85]. The most significant aspect of these reports is the much lower temperature of ceria nanoparticles processing compared to the earlier published literature data and also without any additional external energy source or sophisticated equipment. A simple soft chemical processing route has been employed here. When ball-milling was employed to the hydrothermal technique in the preparation of ceria–zirconia nanoparticles, the particles size was further reduced [85].

Multi-component oxides like spinel phase Co-, Co–Zn and Ni–Zn ferrite nanoparticles have been prepared using microwave-hydrothermal method. The average particle size obtained by such a process is about 10 nm. In the Co-ferrite system, single-phase ferrites with a spinel structure began to form at a relatively low temperature (100 °C) in a short holding time (30 min). Figure 11 shows TEM images of $Co_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Zn_xFe_2O_4$ nanoparticles obtained using microwave-hydrothermal method [86].

Using the mechanochemical-hydrothermal method hydroxyapatite biomaterials have been prepared by several researchers. Figure 12 shows the TEM image of carbonate substituted hydroxyapatite nanoparticles obtained from mechanochemical-hydrothermal method. It is well known that magnesium and carbonate are the two main ionic substitutions in biological apatites, and their preparations carry a great significance for biomedical applications. Such magnesium and carbonate substituted hydroxyapatites have been prepared using via heterogeneous chemical reactions under ambient temperature with the help of mechanochemical-hydrothermal route [87].

During mid 1990s, the influence of biomolecules in nanomaterials synthesis was reported by several researchers [88, 89]. In this special edition Komarneni et al. are reporting the synthesis of one-dimensional (1D) nanorods/nanowires and assemblies of inorganic materials with the assistance of biomolecules (such as sugars and their derivatives; amino acids and their polymers, peptide and protein) under conventional- or microwave-hydrothermal conditions [90]. Similarly a great variety of magnetic nanoparticles, phosphors and quantum dots have been prepared using the hydrothermal processing method.

CNT in 1991 has opened a new era in materials science and nanotechnology research by S. Ijima [91]. CNTs show outstanding electrical and mechanical properties. They are potential building blocks for microelectronics and macro-nanoelectromechanical devices [92]. Most of these applications require CNTs in some kind of alignment in order to use them as field effect transistors, electron-field emitters, etc. In view of the large number of well-defined carbon–carbon single and double bonds in most carbon nanotubes, carbon nanotube at its very essence is polymeric. Having a conjugated all-carbon structure, carbon nanotubes have indeed been demonstrated as possessing some similar

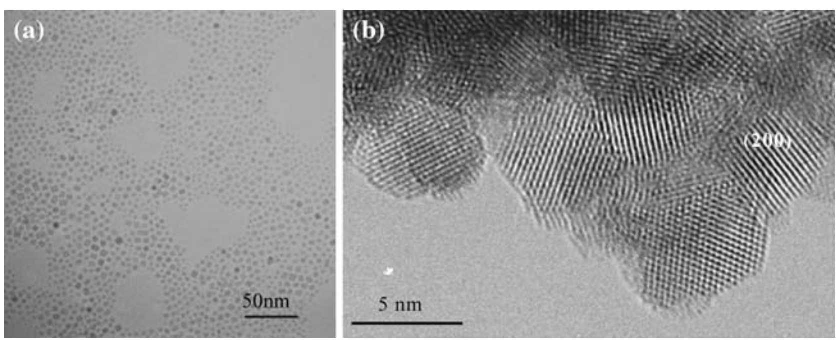


Fig. 10 TEM images of soft hydrothermally processed: (**a**) ceria nanoparticles; (**b**) ceria–zirconia nanoparticles [84, 85]

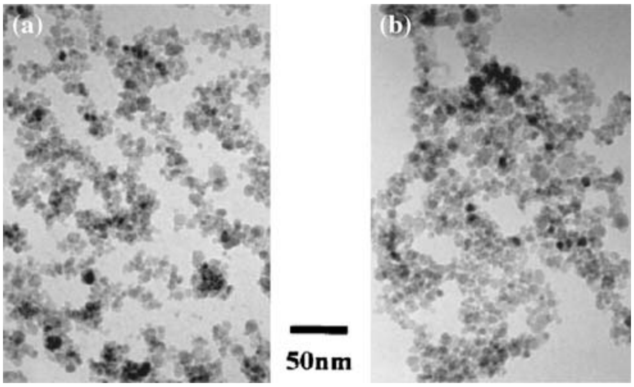


Fig. 11 TEM images: (**a**) $Co_{1-x}Zn_xFe_2O_4$; (**b**) $Ni_{1-x}Zn_xFe_2O_4$ nanoparticles obtained using microwave-hydrothermal method [86]

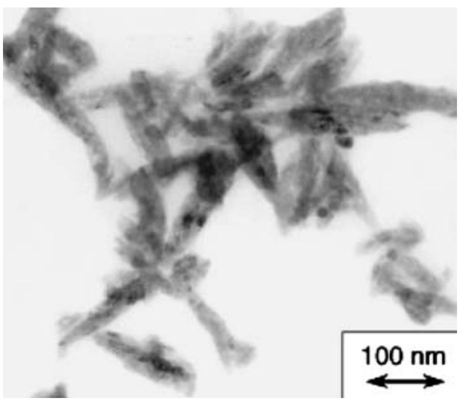


Fig. 12 TEM photograph of the as-prepared carbonate substituted hydroxyapatite from mechanochemical-hydrothermal method [87]

optoelectronic characteristics to conjugated polymers. Just as conjugated polymers have widely been regarded as quasi-one-dimensional semiconductors, carbon nanotubes can be considered quantum wires [93, 94]. The interesting electronic and photonic properties, coupled with their unusual molecular symmetries have made carbon nanotubes very attractive for many potential applications including single molecular transistors, scanning probe microscope tips, gas and electrochemical energy storage, catalyst, protein/DNA supports, molecular-filtration membranes and artificial muscles. Water dispersible carbon nanotubes can be used as 'nano-needles' for the injection of DNA into cells [95, 96]. There are two types of carbon nanotubes: single wall carbon nanotubes (SWCNT) and multi-wall carbon nanotubes (MWCNT). The MWCNs possess strong bonding properties that are ideal for forming biocompatible composites. The multi-functionalization of CNTs finds application in the design of systems for delivery of antibiotics to different type of cells. Since CNTs have high surface energy, they can be used as next generation biomaterials for neural prosthesis at the nanometer scale. Some attempts have been made by researchers using CNTs of diameters similar to those of small nerve fibres, they developed methods for growing embryonic rat-brain neurons on MWCNTs [97].

The most popularly used method of preparing carbon nanostructures is the CVD method in the presence of a catalyst metal. However, the pyrolysis of hydrocarbons is also used. They yield poorly ordered crystals and need the presence of nanosized metal particles acting as catalyst. A similar growth mechanism is used in the gas phase also in high temperature regime and vacuum or inert atmospheres. Hydrothermal routes may lead to a reproducible fabrication method of crystalline nanoforms of carbons with a control over the structure and morphology, which is very essential especially in case of carbon nanotubes. The hydrothermal technique is one of the solution processing methods. It is rather easier than gaseous processes, where highly energetic species like vapours, molecules, atoms and/or ions are used as diluted gaseous media. Further, in gaseous processes, not all the gas(es) and heat are used in the production of materials, and some amount of that is wasted, since gaseous systems are open systems. Also the recycle of gases is difficult, because gas does not condense by itself particularly in diluted gaseous system with huge volume like vacuum pumping. Whereas in solution processing like hydrothermal, which is essentially a closed system, the recycle of solutions is not very difficult, because liquid is condensed by itself since liquid has much smaller volume than gas. Thus we can say that hydrothermal routes for various nanoforms of carbons are a new area of study, which is rather under milder conditions than the gaseous media. Yoshimura and group have done extensive work on the fabrication and stability of the carbon nanoforms and CNTs in particular under supercritical hydrothermal conditions [98–101]. They suggest that virtually any liquid, solid or gaseous carbon source can be used in the supercritical hydrothermal synthesis. Through an appropriate tuning of the experimental conditions, they were able to obtain carbon nanoforms including CNTs with a wide variance in structure. The experimental conditions used by this group are: T = 550–800 °C; P = up to 100 MPa. Also the stability of the CNTs has been studied extensively under supercritical hydrothermal conditions by the same group. The results show that the SWCNTs completely transform into MWCNTs and polyhedral nanoparticles [102]. It means that the SWCNT (as well as fullerene) is not stable under hydrothermal conditions, but the MWCNTs are very stable. Thus the degradation of SWCNT may occur at medium or moderate temperatures, 500–700 °C in the presence of water, moisture and humidity. Whereas MWCNTs are very stable even under such severe corrosive conditions. Hence, the MWCNTs are more suitable than SWCNTs, in the fabrication of composites like mechanical parts, thermal durability, microwave shielding, electrical conducting, etc. In case of carbon nanostructures fabrication metal carbides, carbon suites and other sources of carbon were used in the presence of organic compounds under hydrothermal conditions. Figures 13 and14 show some of the carbon nanoforms obtained by Yoshimura et al.

Hydrothermal preparation of nanocomposites

The hydrothermal technique is emerging as an important tool to fabricate nanocomposites of various materials with a device potential. A great variety of nanocomposites like TiO_2:CNT, ZnO:Activated carbon, TiO_2:Activated carbon, TiO_2:HAp, zeolites:CNT, ferrites:polymer, organic–inorganic composites, polymer/semiconductor composites, etc. [103–105]. Most of these composites have been fabricated at lower temperature conditions in a few hours duration with the help of appropriate solvent and/or organic ligands. These composites have promising new applications in many fields such as mechanics, optics, electronics, catalysis, and biology. Especially in case of core-shell fabrication in quantum dots, this has a special significance. Figure 15 shows the TEM image of polystyrene/CdS nanocomposites prepared at 100 °C for 12 h (a) and ZnO impregnated onto activated carbon at 150 °C under hydrothermal conditions (b). There are a large number of such advanced nanocomposites fabricated under hydrothermal conditions.

Soft hydrothermal fabrication of ceramic films and patterns

There are several techniques to form fine patterns of 1D or 2D or even 3D structures by depositing materials onto substrates surfaces through physical and chemical methods like CVD, PVD, vacuum deposition, sputtering and plasma methods, etc. These pattern structures are required for various applications in the field of electronics, photonics, magnetics, etc. Most of these conventional techniques consume higher energy in terms of pressure, or temperature, or expensive/sophisticated equipment, high purity expensive gases and multi-step fabrication. In this context, Yoshimura and group have extended the concept of soft solution processing involving mild hydrothermal, or electrochemical-hydrothermal to the *on-site* fabrication of functional ceramics based films and patterning on a variety of substrates including porous substances like filter paper, silicon wafer, organic sheets, etc., in a single step without involving any firing or post-treatment. The basic principle of electrochemical-hydrothermal method has been adapted in the deposition of $LiCoO_2$ films on Teflon membrane substrate using high pH (~14) LiOH solution at 200 °C [106]. Similarly using a simple ink-jet printer cartridge various patterns of PbS, CdS and so on were formed on the filter paper under ambient conditions [107]. The most important of these works is the direct carbon patterning on a conducting substrate in an organic liquid [108]. Here the basic electrolysis of a solvent is carried out using a thin

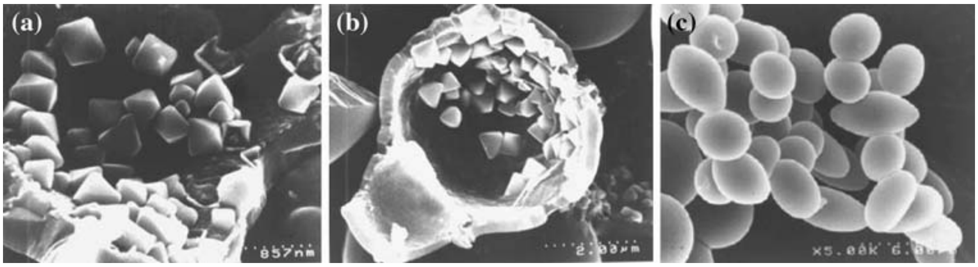


Fig. 13 Carbon nanostructures obtained through the dissociation of metal carbide under supercritical hydrothermal conditions [99]

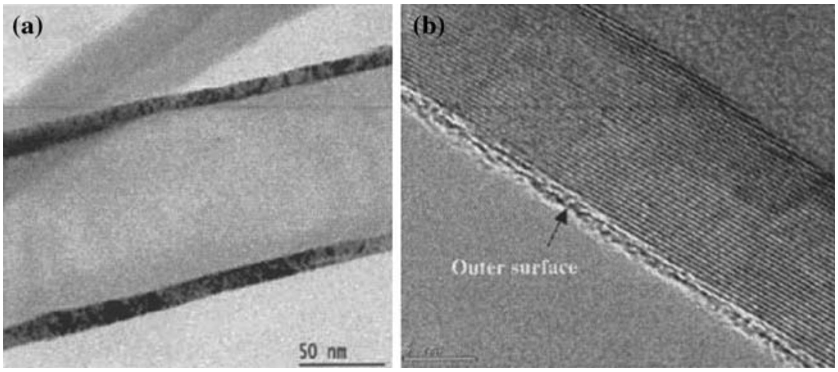


Fig. 14 TEM micrographs of carbon nanotubes produced from PE/water/Ni mixtures. Carbon nanotubes are characterized by a wide channel (95 nm) and thin walls (~10 nm) (**a**). The lattice fringe image (**b**) shows highly ordered graphitic wall structure [101]

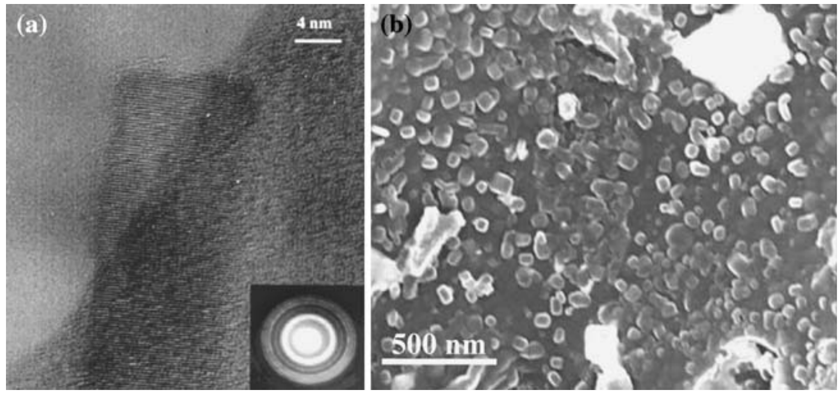


Fig. 15 HRTEM image and electron diffraction pattern (inset) for the PS/CdS nanocomposites prepared at 100 °C (**a**); ZnO impregnated onto activated carbon at 150 °C (**b**) [104, 105]

wire electrode, local Joule heating occurs in the solvent. Under suitable conditions of energy dissipation, an arc discharge might be formed if the applied RF voltage is sufficiently high. This method can produce in the liquid an extreme environment that is closely analogous to those produced by plasma or ionizing radiation [109]. Accordingly, some non-equilibrium reactions may occur resulting in some metastable products. This is the reason for the formation of diamond-like carbon with a part of hydrogenated sp^3 bonded carbon under this condition. Figure 16 shows the direct patterning methods for ceramics: (i) single-step without firing; (ii) normal mask-less patterning methods for ceramics. Figure 17 shows patterns on various substrates. By this means, it is evident that the direct or in situ fabrication of films in/from solutions without firing which was hitherto difficult has been made possible now. The chemical driving forces are used mainly rather than the thermal driving forces. The films and patterns of $BaTiO_3$, $SrTiO_3$, $LiCoO_2$, CdS, $CaWO_4$, etc., could be fabricated at low temperatures (room temperature to 200 °C). A control over the solution flow and/or local activation may produce 2D or 3D patterning.

Future trends in hydrothermal research

Hydrothermal technology, whether it is hydrothermal or solvothermal or supercritical, has a great perspective owing to its multi-faceted advantages in processing of a wide variety of advanced materials starting from bulk single crystals to fine and ultrafine crystals and finally the nanocrystals or nanoparticles. The hydrothermal technology has been revived significantly in the last few years for the growth of most strategic crystals like ZnO, $GaPO_4$, langasite, GaN, etc., as bulk single crystals, followed by the synthesis of diamond, silicon carbide, silicon nitride, ruby, emerald, zoisite, etc. The processing of fine particles and nanoparticles is growing fast as a most attractive tool owing to several advantages in comparison with the conventional methodologies. More recently the concept of multi-energy-hydrothermal technology has been introduced and it is going to play a vital role in future materials processing because of its speed, cost, and convenience and environmentally benign. Here it is very important to note the role played by the chemistry especially, the precursor's preparation for materials processing whether it is

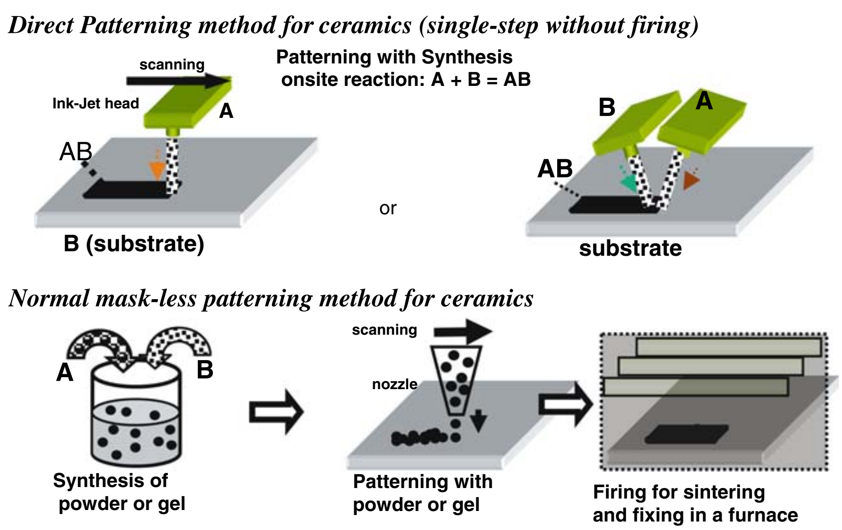


Fig. 16 Direct patterning methods for ceramics [107]

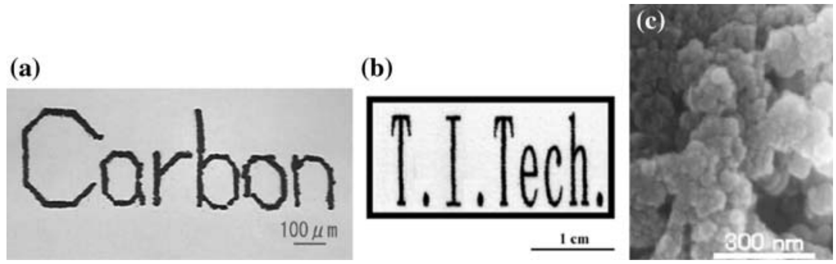


Fig. 17 Single step direct fabrication of patterns: (**a**) carbon films on a silicon wafer; (**b**) patterned letters of PbS on a filter paper; (**c**) CdS pattern fabricated on a filter paper [107, 108]

hydrothermal or other conventional methods. For industrial scale production of materials, the supercritical hydrothermal, particularly the supercritical CO_2 and H_2O will have a greater role to play for a wide range of materials, as they are part of the green chemistry. Also the waste-less processing is the future of materials processing with an eye on the environmentally benign conditions without leading to the global warming. In this context the soft solution processing, which embraces all the set of processes that operate without involving extreme pressure or heat, or vacuum, etc., has a great potential as a materials processing tool. In soft solution processing what is most important is the precursor solutions. Several researchers predict that the combination of polymerizing sol–gel and hydrothermal has a great potential to process materials under environmentally benign conditions. For example, a methodology proposed by Kakihana and Yoshimura [110, 111] like a water-soluble titanium complex for the selective synthesis of brookite, rutile and anatase under hydrothermal conditions will lay a firm foundation for environmentally friendly processing in future. Such an approach has yielded fruitful results to the processing of even high temperature electroceramics like $BaTiO_3$, $SrTiO_3$, etc. Similarly the gel chemistry of metal alkoxides would provide new avenues for precursor preparation for hydrothermal processing of advanced materials. Hence, an interdisciplinary approach will be the most effective solution for the future materials processing strategies, which are environmentally benign and highly cost effective. Hydrothermal technology will be one such most powerful tool in combination with the sol–gel and multi-energy even for the multi-component systems.

Conclusions

Hydrothermal technology has evolved as a most powerful tool in materials processing because it is environmentally benign and highly suitable for advanced materials processing starting from bulk single crystals to fine and ultra-fine crystals and finally the nanocrystals or nanoparticles. The wasteless processing is the future of materials processing with an eye on the environmentally benign conditions without leading to the global warming. Progress in the physical chemistry and solution chemistry of the hydrothermal media leading to the modelling of the hydrothermal reactions have greatly assisted in the intelligent engineering of the materials under much reduced PT conditions. The hydrothermal technique is the only suitable technique to grow large bulk crystals of quartz, berlinite, gallium phosphate, and synthesis of zeolites and other clay materials. The use of multi-energy systems like microwave-hydrothermal, electrochemical-hydrothermal, mechanochemical-hydrothermal, sonar-hydrothermal, etc. drives this technology to a new and totally unexplored avenue in the 21st century. With the additional energy variables in the system, the thermodynamic relationship reads completely different and most complicated. This forms the future of materials processing, which can be termed as novel methods of advanced materials processing. The use of capping agents, surfactants and other organic or biomolecules contributes greatly to the surface modification of these nanocrystals to obtain the desired physico-chemical characteristics. Hydrothermal technology bears a special mention in advanced materials processing through its ability to significantly accelerate the kinetics of synthesis, to model the theoretical approaches from solutions to develop in-situ observation techniques, to evolve SCW and SCF technologies for decomposing and recycling toxic hazardous chemical wastes as well as the monomerization of high polymer wastes and other environmental engineering and chemical engineering issues dealing with recycling of rubbers and plastics instead of burning, etc. The combination of hydrothermal technology and nanotechnology can answer most of the problems associated with advanced materials processing in 21st century. Similarly the combination of polymerizing sol–gel and hydrothermal has a great potential to process materials under environmentally benign conditions. The gel chemistry of metal alkoxides would provide new avenues for precursor preparation for hydrothermal processing of advanced materials. Thus, an interdisciplinary approach will be the most effective solution for the future materials processing strategies, which would be not only cost effective but also environmentally benign. All these advantages present a great perspective for hydrothermal technology in the 21st century for advanced materials processing.

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