

Solvothermal and hydrothermal processes: the main physico-chemical factors involved and new trends

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Abstract Hydro- and solvothermal processes play an important role in the different scientific domains involving either basic or applied research. During the last years, such processes have been strongly developed, in particular with the elaboration of nanocrystallites. This review article presents a brief history of their development, an analysis of the key factors governing such processes, and the recent trends.

Keywords Hydro/solvothermal processes · History of hydrothermal processes · Key factors · New trends

Introduction

Due to the role of water in most mechanisms involved in different natural systems (geology, chemistry, biology, etc.), the first part of this article will be devoted to a brief history of hydrothermal processes.

In the second part, an analysis of the key factors governing such hydro/solvothermal processes will be conducted.

Taking into account the strong development of such processes during the last 20 years, the objective of the third part will be to summarize the recent trends.

The conclusion will propose some trails to improve the development of hydro/solvothermal processes in the near future either for a better understanding of the mechanisms governing these reactions or for the adaptation of these processes to major problems in different scientific domains.

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A brief history of hydrothermal processes

Hydrothermal processes: the overlap between pressure as thermodynamical parameter and the specific properties of water

After the definition of pressure during the 17th century as a thermodynamical parameter, in particular by Pascal in the paper “*Traité de l'équilibre des liqueurs*” published in 1663 [1], different research areas involving this parameter were developed: (i) in physics, with the studies involving the compressibility of gases and liquids, conducted by Andrews [2], Amagat [3], Cailletet and Mathias [4], (ii) in geology, with the research focusing on the synthesis of natural minerals, in particular the experiments of Hall at the end of the 18th century [5], (iii) in hydrometallurgy [6] with the elaboration processes of different metals by Beketoff [7] and Ipatiev [8], and then (iv) in biology at the end of the 19th century, with the discovery of living organisms in the deep sea with Regnard [9] and Certes [10] and then the first pressure experiments dealing with the inactivation of bacteria conducted by Roger [11] and Hite [12].

All these scientific domains took into account the impact of water under high pressure. Therefore, the development of hydrothermal processes resulted from the overlap between pressure, the specific properties of water in such conditions, and chemistry.

The so-called “hydrothermal processes” can be defined as a chemical reaction in a closed system involving one or different precursors in the presence of water at a temperature higher than its boiling temperature. Due to these conditions, pressure is involved. Consequently, the first research in geochemistry was entitled “*Minerals in hot water*” [5].

The first developments of hydrothermal processes in geochemistry

Hall, taking into account Hutton’s proposition that pressure was the solution to retain CO₂ during the fusion of minerals, succeeded in transforming chalk to marble. Such experiments led to the publication in 1805 of the paper: “*Account of a series of experiments showing the effects of compression in modifying the action of heat*” (Hall 1805) [5].

Hall’s experiments inspired a group of French mining engineers and geochemists: de Senarmont (1808–1862), Daubree (1814–1896), and Friedel (1832–1899) [5].

The first high-pressure equipment was developed in glass ampoules filled to 50% of their volume with water and submerged in brass gun barrels also containing water as the pressure-transmitting medium. The barrels were placed at the top of the gas furnace of a foundry (200–300 °C) and covered with coal dust [13]. Due to the experimental difficulties for the management of these experiments, the gun barrels were rapidly replaced by steel bombs as reaction vessels [14]. Then, Friedel and Sarasin (1879) initiated extensive hydrothermal studies in particular with the synthesis of orthoclase from potassium silicate and AlCl₃ [15].

During approximately the same period, Schafhäütl (1803–1890), with the preparation of quartz microcrystals through the transformation of freshly precipitated silicic acid in a Papin's digester [16], Bunsen (1811–1899) with the use of thick-walled glass tubes allowing to reach 100–150 atmospheres (10–15 MPa) [17, 18], Von Chrustoff [19], and Doelter (1890) [20] were involved in hydrothermal geochemistry.

All these scientific works can be considered as the early developments of the hydrothermal processes and the basis for all research conducted from the end of the 19th century to 1950.

The diffusion of hydrothermal processes in different scientific domains

From the end of the 19th century to the middle of the 20th century, different scientists developed hydrothermal reactions mainly in the crystal growth of α -quartz (Spezia [21–23], Nacken [24, 25], Walker [26], Wooster and Wooster [27], Brown et al. [28], Hale [29], Buehler and Walker [30], Shaftal and Butsov in [31], Taki and Kunitomi [32], see also the review of Moriya and Ogawa [33]) and in the systems silicates-H₂O (Katsurai [34], Nagai [35], Yamasaki and Titani [36], Niggli and Morey [37], Straub [38], Morey and Ingerson [39], Goranson [40], Barrer [41], Kiyoura [42], Bowen and Tuttle [43], Barrer and White [44–46], Kennedy [47], Otsubo and Kato [48], Kunitomi and Saito [49], and Roy and Osborn [50]).

All of these research activities were driven by the development of hydrothermal equipment. The development of sealed glass ampoules as “hydrothermal reactors” was improved in particular by Allen et al. [51]. Different apparatuses for the hydrothermal synthesis and growth of single crystals were set-up, in particular by Morey [52], Smith and Adams [53], Tuttle [54], Litvin and Tules [55], and Butusov and Bryatov [56].

During the second part of the 20th century, different research groups were involved in the development of hydrothermal processes either in materials chemistry (synthesis of new materials) or in materials science (crystal growth—even at the industrial scale, elaboration of small crystallites—from micro to nanoscale, the deposition of thin films), particularly by: Somiya and Roy [57], Roy and Tuttle [58], Roy and Osborn [50], Fyfe [59], Yamasaki et al. [60, 61], Koizumi and coworkers [62], Laudise and Nielsen [63], Somiya [64, 65], Yoshimura et al. [66, 67], Demianets [68], Demianets and Lobachev [69], Eitel [70], Rabenau [71], Joubert and coworkers [72], Demazeau and coworkers [73, 74], Whittingham and coworkers [75], Komarneni and coworkers [76, 77], and Riman et al. [78].

At the beginning of the 1990s, after the oxides “era” and the beginning of non-oxide ceramics and in particular the synthesis of nitrides, for example, non-aqueous solvents were developed. Therefore different appellations were used for the corresponding reactions using these solvents in a closed system such as ammonothermal [79], glycothermal [80], alcohol-thermal [81]. Demazeau and coworkers [82, 83] proposed the word “solvothermal” as a generic appellation including all solvents.

Over the last 10 years, different trends have arisen from all the previous investigations, including: (i) the strong improvement of solvothermal processes in

different scientific domains, in particular nano-systems, and the very prolific activity of several research groups in China, and (ii) the optimization of these processes thanks to the analysis and control of the key factors governing each step.

Key factors governing hydro/solvothermal processes

The role of the solvent in solvothermal process

The role of the solvent in the solvothermal synthesis involving oxides and sulfides in particular has been the subject of several investigations [84].

The solvent is involved through: (i) its physical properties (dielectric constant, polarity, density, etc.), (ii) its chemical properties (mainly the solvation and the ability or not to stabilize complexes), and (iii) its interactions with the reactants and the additives.

Role of the solvent in materials chemistry

In materials chemistry, the selection of the solvent mainly depends on the purpose of the experiment: for example, *to help the formation of a specific material* through the control of either the solvation of the chemical reactive species or the concentration of the reactants using in particular non-miscible mixed solvents.

In the case of the solvation, the synthesis of KTaO_3 with the perovskite structure in non-strong alkaline solutions can be chosen as an example. In hydrothermal processes using Ta_2O_5 and KOH as reactants, the hydroxyl ion activity is a critical parameter for the formation of the perovskite KTaO_3 phase. Consequently, the hydrothermal synthesis of the ferroelectric perovskite KTaO_3 requires a high concentration of KOH (=15 mol/l) [85].

The solvent effect can play an important role in acid and base activity through the solvation phenomenon [86, 87].

In water, the solvation of OH groups, through the formation of hydrogen bonds, leads to a partial shielding of hydroxyl group. Consequently, hydroxyl ion activity can be decreased.

In ethanol, the solvation effect is weaker than in water and then induces a higher OH activity. Therefore the chemical reactivity of KOH in ethanol would be improved. He et al. [88] have observed that the hydrothermal synthesis of the KTaO_3 perovskite in pure ethanol required only a concentration of KOH close to 1 mol/l (far below the 15 mol/l used in water).

In the case of non-miscible solvents, one objective is to govern the concentration of the reactants or one specific reactant in the droplets (used as tiny reactors) of one solvent, the size of such droplets being governed by the volume ratio of solvents. This approach has also been used for the preparation of KTaO_3 with the perovskite structure.

The reactants KOH and Ta_2O_5 , being only soluble in water when a mixed—solvent, H_2O /hexane is used, the KOH concentration in water droplets (as tiny reactors) can be adjusted by the ratio between the volumes of water and hexane [88].

Another example is to orient a specific structural form for the final product. For this application, the control of the kinetics governing the formation of the final product is important. Using the same precursors, MnCl_2 , $4\text{H}_2\text{O}$, and $\text{SC}(\text{NH}_2)_2$, several solvents (water, ethylenediamine, ammonia, benzene, THF) were evaluated for their ability to induce a specific structural form for MnS. The stable α form with the rocksalt structure is observed with solvents able to stabilize an intermediate complex $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Mn}(\text{en})_3]^{2+}$, $[\text{Mn}(\text{NH}_3)_6]^{2+}$. On the contrary, metastable structures are observed when the Mn^{2+} complexation is not possible: the γ form (wurtzite structure) with THF and the β form (zinc-blend structure) with benzene. The stable α rocksalt structure results from the lower kinetics induced by the intermediate complex. The difference between benzene and THF has been attributed to the difference of polarity between these solvents, such a difference being able to modify the assembly of atoms [89].

Role of the solvent in materials science

In materials science, three main domains have been investigated: (i) the elaboration of nanoparticles with the control of their size and morphology, (ii) the solvothermal growth of single crystals, and (iii) the elaboration of nanocomposites.

The control of the size and morphology of fine particles Two main routes have been developed using solvothermal reactions:

- *The control of the nucleation step* using the physical properties of the solvent in particular (for example its critical temperature value). Hakuta et al. [90, 91] reported the preparation of YAG powder doped with Tb by a hydrothermal process (water being used as solvent) at 400 °C and 30 MPa. Recently Li et al. [92] described the preparation of the same Tb-doped YAG phosphor particles using a mixed solvent (ethanol/water). The experimental conditions are slightly reduced (300 °C, 10 MPa) compared to the ones used in pure water. Such a difference has been attributed to the lower supercritical conditions corresponding to a mixed solvent: ethanol–water 2:1 (267 °C, 7.5 MPa) compared to (374 °C, 22 MPa) for pure water. The solubility of metal oxides and hydroxides decrease drastically above the critical point and consequently the nucleation of YAG crystallites takes place at a lower temperature in such a mixed solvent. This example illustrates the role of critical conditions on the solvothermal preparation of small crystallites.
- *The control of the crystal growth step*
Two different aspects have been particularly explored.
 - *The formation of an intermediate compound used as template to orient the morphology of the final material.*
For the solvothermal synthesis of one-dimensional metal selenide crystallites, using metal chlorides (or nitrates) and selenium powder as reactants and hydrazine hydrate as the solvent, the hypothesis that the “ NH_2NH_2 ” group could act as bidentate ligand between two different M^{n+} cationic

clusters has been postulated. Such intermediate chemical species could then induce the one-dimensional morphology of the resulting particles [93].

- *The selection of the solvent with the appropriate physico-chemical properties.*

Indium–titanium oxide (ITO) has been prepared through a solvothermal process using hydrated indium nitrate [$\text{In}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$], tin (IV) chloride [$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$] as reactants and NH_4OH as the mineralizer. The resulting precipitate, after drying, was treated under solvothermal conditions (250 °C, autogeneous pressure) using different solvents: ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), polyethylene-glycol [$\text{H}(\text{OC}_2\text{H}_4)_n\text{OH}$], and ethanol [$\text{C}_2\text{H}_5\text{OH}$]. Through a TEM analysis of the resulting material, solvent viscosity seemed to play an important role in the size and the physico-chemical properties of the resulting ITO crystallites. The increase of the viscosity [from $\text{C}_2\text{H}_5\text{OH}$ to $\text{H}(\text{OC}_2\text{H}_4)_n\text{OH}$] improved the crystal growth rate compared to the nucleation rate and, in parallel, induced the formation of oxygen vacancies leading to more free electrons and higher conductivity [94]. The role of the viscosity of the solvent has also been underlined for the morphological control of rare earth oxide nanoparticles by solvothermal reaction [95].

The solvothermal growth of single crystals The hydro- and solvothermal growth of bulk single crystals was an important step in the development of such processes.

During the last 10 years, the solvothermal crystal growth of sulfide materials has been an important challenge due to the potential developments of this class of materials for different applications [96–98].

Manganese sulphide (MnS) crystallites were prepared from MnCl_2 , $4\text{H}_2\text{O}$, thiourea ($\text{CS}(\text{NH}_2)_2$), CS_2 being the solvent and KOH or KNO_3 as the mineralizer at 200 °C during 10 h.

The γ -form of MnS was observed. The presence of the mineralizer KNO_3 improved the crystallization of the manganese sulphide. Substituting KOH for KNO_3 as the mineralizer, the α - MnS form was stabilized. The solvent CS_2 , associated with such a mineralizer, appeared to modify the structural form, crystals morphology, and to improve the crystallinity [99].

The elaboration of nanocomposite systems Nanocomposite systems can be defined as the uniting of different nano-components.

A novel strategy has been recently proposed to synthesize metal-oxide nanotubes through the homogeneous coating of carbon nanotubes (CNTs) through a solvothermal process. For example, using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the precursor, different solvents [ethanol, dimethylformamide (DMF), toluene, pyridine] were investigated for the preparation of CeO_2 nanotubes [100]. The formation of a uniform CeO_2 deposit on CNTs was only observed when pyridine was chosen as the solvent. This phenomenon may be related to N present in pyridine that could be able to modify the surface of CNTs in the earliest stage in order to facilitate the CeO_2 deposition.

Some bionanocomposites were also prepared with layered substrates such as mica or different inorganic matrix with intercalation of biomolecules in the interlamellar spaces [101].

In addition, the physico-chemical properties of the solvent can be modified through (a) the use of additives, and (b) the values of the thermodynamical parameters of temperature and pressure (with temperature, the physico-chemical properties are strongly modified depending on whether it is a subcritical or supercritical domain).

Impact of additives in solvothermal processes

Additives are generally developed to modify either the properties of the solvent or one step of the process. For example, they are important for modifying:

- (i) the solubility of the reactants with the use of mineralizers;
- (ii) the oxidation–reduction properties;
- (iii) the crystal growth using either capping agents, surfactants, or biomolecules to orient growth to obtain an anisotropic morphology (for example, ethylene glycol can also play the role of capping agent for preparing hierarchical FeWO_4 microcrystals [102]).

Role of the thermodynamical parameters of temperature and pressure

The main impact of temperature in solvothermal processes

The main impact of temperature in solvothermal processes is to differentiate two different domains where the physico-chemical properties of the solvent are modified: the subcritical and the supercritical domains [103].

Temperature is a key parameter of all solvothermal processes and can be adjusted to:

- (i) stabilize a specific structural form of the final material, such as in the case of the solvothermal synthesis of hybrid vanadium oxyfluorides [104];
- (ii) modify the oxidation state of transition elements, for example the $n+$ value for V^{n+} in the case of oxyfluorides prepared in the Na-V-(O)F and K-V-(O)F systems by solvothermal methods [105]. If V^{4+} oxyfluorides are prepared at 100 °C, only V^{3+} fluorides are obtained at higher temperature as 220 °C;
- (iii) optimize the size and shape of nanoparticles by increasing the temperature or reaction time. For example, the size and the crystallinity of the resulting CdS nanorods are improved [106].

The role of pressure in solvothermal processes

The role of pressure in solvothermal processes has not yet been extensively investigated as the autogeneous pressure value commonly being used. In the solvothermal crystal growth of α - quartz, a specific evaluation of the impact of

pressure on the concentration of chemical defects has been investigated [107]. Due to the compensated substitution $\text{Al}^{3+} \rightarrow \text{Si}^{4+}$ and $\text{OH}^- \rightarrow \text{O}^{2-}$, the IR coefficient α_{3500} (corresponding to the maximum IR absorption for OH groups) is used to estimate the concentration of chemical defects. The decrease of α values with increasing pressure underlines the role of this parameter on the Al^{3+} insertion into the $\alpha\text{-SiO}_2$ lattice.

Impact of the pH of the solution

The pH value can play different roles in solvothermal processes for:

- (i) the preparation of specific materials [108];
- (ii) the stabilization of different structural forms [109];
- (iii) the control of the size and morphology of crystallites:
 - through the modification of the decomposition of one reactant [110];
 - through the change of the ionization equilibrium of the additive [111];
- (iv) and the elaboration of nano-composites [111].

The selection of the reactants

The choice of the reactants can affect the final product because of their different characteristics, such as:

- the chemical composition of one reactant used as a specific chemical source;
- the structure of the reactant to orient one of the final product;
- and the general composition of the reaction medium (ratio of the reactants).

The role of chemical composition

Using thiosemicarbazide as the starting sulphur source, CdCl_2 as the cadmium precursor and ethylenediamine as the solvent, CdS nanowhiskers were obtained. Such elongated nano-crystallites would be generated through the attack of the thiosemicarbazide molecules by the strong nucleophilic nitrogen of ethylenediamine leading to the weakening of the C=S double bonds. The rupture of C=S being slow, the reaction rate is also slow and contributes to the lengthening of CdS crystallites [112].

The selection of Fe-oleate precursors can induce the formation of seed-nanocrystals able to improve the crystal growth of iron oxide nanoparticles [113].

The structural form of the reactant

In most cases, solvothermal processes involve the dissolution of the reactants. If one of the reactants remains in the solid state under solvothermal conditions (in particular for low-temperature synthesis), it becomes possible to initiate the structure of the final product through one of the insoluble reactants. Such a

solvothermal route was called “structure-inheriting solid-state reaction” by Whittingham and coworkers [114]. The effect of the reaction time during the synthesis of CoMoO_4 through a solvothermal process (using water as solvent) was investigated at 453 K using MoO_3 and CoO as precursors.

The composition of the reaction medium

Under ambient pressure and temperature conditions, NaYF_4 is characterized by two structural forms: the cubic (fluorite type) and the hexagonal ($\text{Na}_{1.5}\text{Nd}_{1.5}\text{F}_6$ type) structures, depending on the preparation method. NaYF_4 has attracted great interest due to its potential use as host lattice for up-conversion phosphors [115, 116].

Y_2O_3 and NaF were used as the precursors and EDTA (ethylenediamine tetraacetic) as the complexing agent and water as the solvent.

Depending on the Y^{3+}/F^- ratio, the cubic form was stabilized with a stoichiometric ratio and the hexagonal one for an excess of F^- ($\text{Y}^{3+}/\text{F}^- = 1/7.5$). The F^- concentration played an important role on the stabilization of the structural form, the EDTA/ Y^{3+} ratio governing mainly the morphology. In such a synthesis, F^- acts both as the reactant and as the mineralizer [117].

The associated technologies

The associated technologies (electrochemistry, microwaves, mechanical mixing, ultrasounds, external magnetic field, etc.) are able to improve the kinetics of solvothermal reactions of one or two orders of magnitude [118] or to induce a specific morphology of magnetic crystallites [119]. These associated technologies have been developed in particular for the preparation of well-defined nano-crystallites.

The control of different reaction mechanisms

Over the last 15 years, different reaction mechanisms have been investigated, such as:

- (i) the solvothermal pressure-relief process during which the produced gas into the high-pressure vessel is controlled [120];
- (ii) the solvothermal scission-template-transportation route with the formation of an intermediate compound acting as the template [121];
- (iii) the extraction solvothermal method [122];
- (iv) and the phase-transfer catalysis [123].

Recent trends in solvothermal processes

Over the last years, some specific trends have been defined for the improvement of solvothermal processes, in particular through the control of the reactions and the preparation of specific material either as nano-crystallites or single crystals. In most

cases, these trends are triggered by the development of these processes for industrial applications.

The control of solvothermal reactions

In order to manage solvothermal processes, new solvents have been developed such as ionic solvents due to their physico-chemical properties but also as directing agents [124], organic solvents [125], or some mixed solutions [126].

In parallel, several reaction mechanisms have also been investigated, such as the controlled reduction method [127], the fluorination process [128], the hot-press method [129], the resin-assisted synthesis [130], the synthesis under external magnetic field [119], and the interdiffusion process for the preparation of nanotubes [131].

The preparation of specific materials

As specific materials, we can consider materials with a macro- or a nanosize:

- with a particular composition (for example the extension from oxides systems to fluorides [132], sulphides [133, 134], sulphate–fluorides [135], nitrides [136, 137], hybrids [138], carbon-systems [139], metallic systems [140], metal–organic frameworks [141], etc.);
- with the synthesis of specific structures, such as perovskite or pyrochlore, in mild conditions [142];
- with some specific characteristics in size but mainly in morphology such as nanotubes [127], fibrous systems [143], nano-composites [144];
- with a specific application (as nanophosphors) [145, 146],
- nano-composites associating different classes of materials (such as carbon and oxides) [147].

The solvothermal growth of single crystals for industrial development initiated important works in particular with GaN and ZnO [148–152]. In this domain, the research focused on three main goals: (i) the improvement of the kinetics for the solvothermal crystal growth, (ii) a lower concentration of defects (chemical defects such as impurities or physical defects such as dislocations), and (iii) the economical cost of the solvothermal process compared to the conventional ones (in particular in the case of ZnO).

The development of specific processes (green chemistry, synthesis of prebiotic molecules, wastes retreatment, etc.)

Hydrothermal processes in green chemistry

In the future, the increase of the earth's surface temperature is one of the major concerns. This is in part due to CO₂ emission from fossil-fuel combustion. The sequestration of CO₂ could be achieved through its transformation to organic components able to be used as basic products [153]. This is why during these last years, hydrothermal processes based on CO₂ have been developed [154, 155].

Another domain of application for hydrothermal processes deals with the production of bioethanol and biofuel [156].

Hydrothermal synthesis of prebiotic molecules

Hydrothermal processes have been considered a possible explanation for the origin of life [157]. Consequently, this route is continuously explored [158].

Hydrothermal post-treatments

Solvothermal post-treatments were developed either for the control of the preparation of specific materials or for the conversion of wastes.

In the first case, the control of the crystal structure of titanium dioxide through the hydrothermal treatment of titanate nanotubes under acidic conditions can be an interesting illustration [159].

Concerning the hydrothermal retreatment of wastes, this topic (initiated in particular by Yamasaki) is still under investigation [160].

Continuous solvothermal processes

The development of continuous solvothermal processes is an important challenge from an economical point of view. During the last years, different nanoparticles have been prepared by this means [161–163].

Conclusions

Solvothermal processes are important in different scientific areas involving both basic research and industrial applications.

In order to improve such processes in the near future, four main domains need to be investigated:

- the potential development of different solvents (including aqueous solutions) through a better understanding of their physico-chemical properties;
- the investigations involving the evolution of the physico-chemical properties of these solvents in the reaction conditions;
- a better knowledge of the in situ chemical mechanisms governing the formation of the target material;
- and the impact of different parameters (in particular pressure) to control the reaction mechanisms.

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