Solvothermal processes: new trends in Materials Chemistry

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Abstract. Solvothermal processes are characterized by mild temperature conditions. The use of high pressure appears important for enhancing chemical reactivity. The roles of the solvent and the reagents in the mechanisms governing the formation of a specific material are underlined. Some new directions of research, at the interface with others scientific domains, are discussed.

1. Introduction
Solvothermal processes can be described as a reaction or a transformation of precursor(s) in presence of a solvent in a close system and at a temperature higher than the boiling temperature of the solvent; Consequently at least autogeneous pressure parameter is involved. Versus the respective chemical properties of the precursor(s) and the solvent such a system can be homogeneous (if the precursors are soluble in the corresponding temperature and pressure conditions) or heterogeneous (if the precursor is partially soluble in such conditions). Very often in order to improve such a solubility an initial high pressure is used. Versus the temperature, the system can be in subcritical and supercritical conditions.

The most developed solvent was water due to its presence at the surface of the earth and its specific role in geochemistry. Different objectives have been assigned to hydrothermal processes: (i) to investigate the elaboration of different natural materials in order to improve the knowledge in Earth-Science [1,2], (ii) to develop hydrometallurgy for recovering ores [3], (iii) to synthesize novel materials, very often metastable when the kinetical effects were predominant [4-10], (iv) to prepare single crystals of oxides – in particular that corresponding to low-temperature structural varieties [10], (v) to elaborate fine particules as micro- or nanocrystallites [11-16].

During these last twenty years non-aqueous solvents were developed for preparing in mild conditions oxides or non-oxides materials through solvothermal processes – mainly as fine particles with specific size and shape for different applications.

Solvothermal reactions are governed by different factors:
- the nature of the precursors, in particular their physico-chemical properties (solubility, thermal stability…),
- the nature of the solvent (chemical composition, physico-chemical properties (solvatation, polarity, viscosity, ability to stabilize some complexes as intermediate steps…),
- the thermodynamical properties used during such a process (pressure and temperature). Pressure and temperature can play an important role, some properties of the solvent such as density, viscosity…, changing drastically versus such parameters. Consequently the diffusion and reactivity of chemical species can be strongly affected. In a general way, solvothermal processes were developed in mild temperature conditions.
The main chemical reaction-types involved in solvothermal processes are: hydrolysis, complex-formation, metathesis, oxidation-reduction… The reaction-type governing the in – situ mechanisms is closely related to the optimization of the three main factors governing the process. (chemical nature of the precursors, physico-chemical properties of the solvent, thermodynamical conditions). Such an optimization
depends on the final objective: synthesis of a novel material (thermodynamically stable or metastable), preparation of fine crystallites well defined in size and morphology, growth of single crystal….

The objective of such a paper is to underline the role of the solvent and that of the reagents in the mechanisms governing solvothermal reactions.

2. Role of the solvent in solvothermal processes
Solvant, through its physico-chemical properties, plays a key role in solvothermal processes. Four examples can illustrate such a role: (i) the orientation of the structural form, (ii) the development of a specific shape for nanocrystallites, (iii) the formation of specific metastable compounds through template action, (iv) the role of the oxidation – reduction properties characterizing the solvent.

2.1. Orientation to a metastable structural form: MnS with the wurtzite or zinc blende structures
Using MnCl₂, 4H₂O and SC(NH₂)₂ as reagents, the stabilization of a specific structural form for MnS has been recently studied [17]. With a solvent able to form a stable Mn complex (water or ethyldiamine), the thermodynamically stable form (α-MnS with the rocksalt structure) is prepared. With a non polar solvent as benzene the formation of the wurtzite-type structure is observed (γ-MnS). On the contrary with tetrahydrofurane (THF) the zinc-blende structure (β-MnS) is stabilized. If during the synthesis mechanisms the formation of a stable complexe (Mn(H₂O)₆⁺ or Mn(en)³⁺) as an intermediate step leads to the stable structural form on the contrary it appears that with benzene or THF the metastable forms (γ or β) can be stabilized, the solvothermal reaction being kinetically control, the orientation toward wurtzite or zinc-blende seems to be correlated in a first analysis to the polar character of the solvent.

2.2. Preparation of nanoparticles with a specific morphology: intermetallic FePt nanowires
The solvothermal preparation of FePt nanoparticles characterized by a one-dimensional (1D) nanostructure has attracted intensive research due to its potential applications in high-density data storage and high performance permanent magnets [18,19]. In the main developed processes FePt particles were synthesized via thermal decomposition of Fe(CO)₅, reduction of platinum acetyl acetonate (Pt(acac)₂) and co-reduction of iron salt and Pt (acac)₂ [20-23]. Unfortunately the morphology of the resulting nanocrystallites is difficult to control. Due to the flexibility of solvothermal routes, such a process has been developed. Ethylenediamine was selected as solvent due to its ability to form a stable complex ion with Platinum [Pt(en)₂²⁻] then a co-reduction of such complex ion through the thermal decomposition of Fe(CO)₅ led to the formation of FePt nanowire [24]. Recently Y. HOU et al. [25] have investigated the solvothermal growth process through TEM observation of the corresponding samples quentched at different reaction times. Starting from aggregated small particles with short rod morphology acting as nuclei, a continual transformation through coarsening and ripening reactions is observed. The whole transformation to 1D nanowires at a temperature close to 180°C can be compared to the surface reconstruction phenomena discovered previously for Pt and its alloys at high temperatures in presence of reactive gases (NH₃ and oxygen) [26,27]. Such a study underlines the importance of the reaction mechanisms for controlling the resulting morphology and the role of solvothermal reactions for reducing the temperature.
2.3. Formation of metastable compounds complex ions acting as template
The solvent through the formation of very stable complex ions can participate to the final composition. Ethylenediamine has a strong coordination ability towards the divalent metal ions as Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$. These complex ions (M(en)$_n^{2+}$) are characterized by an octahedral geometry acting as template for the building of the resulting structure [28].

2.4. Oxidation – reduction properties of the solvent and the preparation of sulfides
S.K. PANDA et al. [29] have underlined the role of the oxidation-reduction process induced by the solvent during the solvothermal synthesis of SnS crystallites from Sn metal and thiourea as reagents. The first step of the reaction mechanism being the oxidation of tin (Sn$^0 \rightarrow$ Sn$^{2+} + 2e^-$), the use of pure ethylenediamine as solvent – due to its slightly reducing properties – does not oxidize Sn metal. The addition of few amounts of water induces the oxidation of the Sn surface and leads to the formation of SnS through the following steps [Sn$^{2+} + n\text{en} \rightarrow \text{Sn(en)}_n^{2+}$ then $\text{Sn(en)}_n^{2+} + S^2- \rightarrow \text{SnS}$].

3. Role of the reagents in solvothermal processes.
Different examples have been selected for illustrating how the physico-chemical characteristics (chemical composition, structure, size and morphology of the reagents) can play a key-role in the solvothermal processes.

The solvothermal synthesis of the phyllosiloxides – bidimensional oxides, isostructural of the natural phyllosilicates as mica – was only possible through a sol-gel process using alkoxides in a first step, the conventional Solid-State chemical processes leading to a mixture of 3D-silicates [30,31].

The elaboration of the metastable phase Rb$_2$Hg$_3$Te$_4$ through a solvothermal process has been investigated by Li et al. [32]. Using Rb$_2$Te, Hg$_2$Cl$_2$, Te and FeCl$_2$ as reagents and ethylenediamine as solvent, the role of Fe$^{2+}$ as possible reducing agent seems to play an important role for stabilizing Rb$_2$Hg$_3$Te$_4$.

During the solvothermal preparation of CdIn$_2$S$_4$ using CdS, InCl$_3$,4H$_2$O and thiourea as reagents and water as solvent – the morphology of the final CdIn$_2$S$_4$ crystallites is strongly correlated to that of the reagents CdS [33].

4. Main potential developments for solvothermal processes.
In addition of the conventional domains (synthesis of novel materials [4], elaboration of single crystals [34,35], preparation of nanocrystallites [36], solvothermal reactions are able to be developed in different scientific areas: synthesis of hybrid materials – involving not only organic-inorganic systems but mainly in the near future bio-organic/inorganic systems - [37,38], the decomposition and the recycling of wastes [39-41]… For the development of such novel scientific promising domains, the mild temperature conditions playing an important role.

Pressure parameter is able to have also a key role. Due to the low-energy developed in liquid phase (Table) [42] such a parameter does not affect strongly the bio-organic molecules and consequently allows the synthesis of bio-organic/inorganic hybrid systems with potential applications in nano-energy-devices, catalysis…[43].
4. Conclusions
Solvothermal processes have been investigated during these last twenty years. The recent development of non-aqueous solvents has improved the synthesis of different materials (chalcogenides, nitrides, …) mainly as nanoparticles. Three different factors play an important role underlined: the mild temperature conditions, the improvement of the chemical reactivity versus pressure and the limited pollution due to the equipments as close-systems pollution. The overlap of these factors allows to consider solvothermal processes to play a key-role in the future.

5. References
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