Impact of High Pressures in Solvothermal Processes

Gérard DEMAZEAU
ICMCB, site de l’ENSCPB, CNRS-Université de Bordeaux
87 avenue du Dr. A. Schweitzer, 33608 PESSAC-Cedex (France)
E-mail: demazeau@icmcb-bordeaux.cnrs.fr

Abstract. A solvothermal process can be define as a chemical reaction in a close system involving different reactants in presence of a solvent (aqueous or non aqueous) at a temperature higher than its boiling temperature. Consequently pressure is involved. Two different cases are possible: (i) pressure is autogeneous and closely dependent of the percentage of filling for the reaction vessel and of temperature, (ii) pressure is imposed.
Solvothermal processes are governed by different key factors: (i) the composition of the reactants, (ii) the nature of the solvent (in particular its physico-chemical properties), (iii) the additives used and (iv) the thermodynamical parameters: temperature and pressure.
The main objective being to control the chemical mechanisms governing the preparation of the target material the selection of the key parameters is an important challenge for Solvothermal processes.

Solvothermal processes have been developed in different scientific fields as: (i) the synthesis of novel materials –in particular metastable materials with specific physical properties-, (ii) the crystal growth of functional materials for industrial applications, (iii) the preparation of nano-crystallites well defined in size and morphology and nano-composite systems, (iv) the deposition of thin nano-structured films…

During these last fifteen years, pressure was in the major cases an autogeneous pressure (pressure developed in the reaction vessel by only the thermal expansion of the liquid phase versus temperature).

An important challenge for the near future is to evaluate how pressure parameter can help the control of the reaction mechanisms governing the formation of the target product.

1. Introduction
Taking into account the definition of a solvothermal process, pressure can act as an important thermodynamical parameter able to modify the reaction mechanisms and consequently the final material in terms of composition and structure.
Pressure parameter is mainly characterized by three main factors:
- the value of the energy conveyed by pressure by its application to the reaction medium,
- the compression effect,
- the induced chemical reactivity.

The value of the energy resulting from pressure application is directly correlated to the compressibility of the involved medium. If this value is important for gases, on the contrary only a small energy is developed in liquid and solid phases.
Table I gives some energy values resulting from the compression of gas, liquid and solid phases and the comparison of such an energy with the average value of a chemical bond [1]
With water as reference for a liquid phase, it appears that the energy added by compression is small and consequently pressure cannot be considered as an energetical parameter for improving a chemical reaction.

The compressibility, in a liquid medium, is also small compared to a gas phase but in all cases pressure induces chemical reactions corresponding to a negative $\Delta V$ value ($\Delta V$ being the volume difference between the final and the initial states).

The improvement of the chemical reactivity observed in the liquid phase can be correlated to two main factors:

- the increase of the solubility generally observed and consequently the concentration of solvated species in the reaction medium is improved,
- the decrease of the average distance between such solvated chemical species [2].

In addition for non homogeneous system the dissolution/precipitation equilibria at the interface liquid/solid can also play an important role.

2. Impact of pressure parameter in Solvothermal processes.
Through this previous analysis of the different factors characterizing the application of pressure and taking into account that solvothermal reactions can be in sub- or supercritical conditions, what are the impacts of high pressures in such processes?

Solvothermal processes have been developed in different scientific areas involving both basic and applied researches [3], for example:

- synthesis of novel materials,
- development of new processes for preparing functional materials in mild temperature conditions,
- stabilisation of hybrid materials (inorganic/organic, inorganic/biological…),
- the crystal growth in mild temperature conditions,
- preparation of micro- or nanocrystallites well defined in size and morphology,
- elaboration of nanostructured films,
- sintering in mild temperature conditions…..

Considering the added energy correlated to the compressibility of the reaction medium, in supercritical conditions- versus the temperature value - pressure can play a role on the density of this medium and consequently the average distance value between chemical species can be gradually modified. In all cases, it is necessary to take into account that the energy added by temperature for reaching the critical temperature is high compared to that added by pressure.

### Table 1. Energy added by compression versus the nature of the medium compared to the average energy of a chemical reaction [R. H. Wentorf, Jr. Chemical Engineering, Oct. 16, p. 177 – 186 (1961)].

| Pressure (bar) | Medium   | Energy cal/mol |
|---------------|----------|----------------|
| 1000          | gas      | 3000           |
| 1000          | solid    | 1              |
| 10 000        | solid    | 5              |
| 100 000       | iron     | 20             |
| 100 000       | H$_2$O   | 1000           |
|               | chemical reaction | 20 000         |

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In addition for non homogeneous system the dissolution/precipitation equilibria at the interface liquid/solid can also play an important role.
The solvothermal reactions being generally managed in mild temperature conditions, the energy does not appear as a critical parameter.

The compression effect (ΔV<0) is important for orienting the formation of the densest structures.

The increase of the chemical reactivity could be correlated to two phenomena: (i) the improvement of the solubility and consequently the increase of the solvated chemical species[4], (ii) the decrease of the distance between such solvated species [2].

In the case of heterogeneous systems the equilibria at the liquid/solid interface would play also an important role.

3. Some examples of high pressure effects in Solvothermal processes.

In the main cases only autogeneous pressure is used and very often without informations concerning the percentage of filling of the pressure vessel. Consequently no many examples can illustrate the pressure effects on solvothermal reactions.

3-1 Materials synthesis.

The stabilization, through a solvothermal process, of a new family of layered oxides (the phyllosiloxides) isostuctural of the phyllosilicates was only possible in a high pressure range [5]. Figure 1 gives a comparison between the natural phyllosilicates with the mica phlogopite structure KMg₃(Si₃Al)O₁₀(OH)₂ and the new isostructural layered oxide K(Mg₂Al)Si₄O₁₂.

![Figure 1: Comparison of the structures and compositions of the natural mica phyllosilicate characterized by the phlogopite structural type (a), with that of the corresponding phyllosiloxide (b).](image-url)

This phyllosiloxide was prepared in two steps: (i) an alkoxide sol-gel route using Si(OC₂H₅)₄, Al(OC₄H₉)₃, Mg(OC₂H₅)₂ and KOCH₃ as precursors and then (ii) a solvothermal treatment of the resulting amorphous gel (50<P<100 MPa, 600<T<800°C, 48<t<72h using the 2-methoxy-ethanol as solvent). XRD analysis and RMN confirm the structure of the phyllosiloxide [6].
3-2 Crystal growth of functional materials

α-quartz due to its piezoelectrical properties and its low temperature structural form was used as model for the low temperature solvothermal crystal growth processes [7]. The main requirement for the resulting single crystals is a small density of defects (chemical and physical). Recently a specific evaluation of the role of pressure in the concentration of chemical defects has been investigated [8]. Due to the compensated substitution \( \text{Al}^{3+} \rightarrow \text{Si}^{4+} \) and \( \text{OH}^{-} \rightarrow \text{O}^{2-} \), the IR coefficient \( \alpha_{3500} \) (corresponding to the maximum IR absorption for OH groups) is used for evaluating the concentration of chemical defects [9].

The decrease of \( \alpha \) values versus the increase of pressure underlines the role of such a parameter on the \( \text{Al}^{3+} \) insertion into the \( \alpha \)-SiO\(_2\) lattice (Fig.2). This phenomenon was confirmed through a chemical analysis of Al concentration in the single crystal using a Castaing microprobe [8]. The pressure effect on the \( \text{Al}^{3+} \rightarrow \text{Si}^{4+} \) substitution during the solvothermal crystal growth of \( \alpha \)-SiO\(_2\) could be attributed to the difference between the size of these cations in tetrahedral coordination \([r(\text{Al}^{3+})=0.39 \text{Å}, r(\text{Si}^{4+})=0.26 \text{Å}]\) [10].

![Figure 2](image)

**Figure 2**: Influence of the pressure value on the growth-rate of SiO\(_2\)-\( \alpha \) (A) and IR characterization (B)

[Solvothermal growth conditions: Solvent: (NaOH.1M), \( T_{\text{growth}} = 350^\circ\text{C}, \Delta T = 10^\circ\text{C} \), duration: 10 days].

Fig.2(A) underlines that the growth rate of SiO\(_2\)-\( \alpha \) is strongly increased with the pressure. Fig.2(B) shows that the content of hydroxyl groups (OH) and consequently the density of chemical defects \( \text{Al}^{3+} \) is reduced when the pressure value is improved. The combination of these two results confirms that high pressure in solvothermal crystal growth of SiO\(_2\)-\( \alpha \) can play an important dual role either on the improvement of the crystal growth rate or the reduction of chemical defects.

3-3 Preparation of nano (or micro-) crystallites

The preparation of crystallites well defined in size and morphology is an important challenge for different applications [11]. If the morphology is dependent on a large number of factors governing the
reaction mechanisms [12] the size is mainly controlled by two phenomena: the nucleation and the crystal growth. Pressure- through the improvement of the concentration of solvated species in the reaction medium induces generally an increase of the crystal growth leading to larger crystallites. Such a phenomenon has been in particular observed for the preparation of Fe₃O₄[13]. A recent study, involving the synthesis of Fe₃O₄ as monodisperse superparamagnetic nanocrystals from the decomposition of iron oleate in alcohol and using oleic acid as the protective reagent, underlines that high pressure and alcohol as solvent can facilitate the formation of Fe₃O₄ nanocrystals. [14]. Such an effect has been explained by the "compression effect" associated with pressure, because the Fe₃O₄ formation from Fe³⁺ and O₂ is a pressure-decreasing process, the displacement of the chemical equilibrium toward the formation of magnetite can be enhanced by higher pressures.

The control of nanoparticles thin films being an important challenge for different applications: nanoelectronics, magnetic storage devices, sensors, catalysis, antibacterial coatings…, solvothermal method was used for preparing such thin films and coatings [15]. The effect of pressure was evaluated through the change of filling fraction governing the autogeneous pressure in the autoclave. The thickness of the film is improved with increasing pressure. Using a simple mechanism based on the sphere-plate interaction, this sphere-plate interaction appears twice as strong as the sphere-sphere interaction and consequently the tendency is to form monolayers of nanoparticles. An increase of pressure could lead to the formation of thick multilayers films [15].

4. Conclusion
High pressures can play an important role in solvothermal processes either in sub- or supercritical conditions. Unfortunately during these last fifteen years only small research works involving such processes have taken into account this parameter. The development of diamond anvil cells for studying the chemical reactions in sub- or supercritical conditions would be an important tool for improving the knowledge either of the solvents properties or the correlations between pressure and the reaction mechanisms leading to the target product [16].

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