Solvothermal reactions: new trends in Materials Science

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Abstract

Solvothermal reaction can be described as a chemical reaction involving a solvent either in subcritical or supercritical conditions. Such a solvent can act as a chemical component or a fluid phase able through its physico-chemical properties to modify the reaction mechanisms.

During these last twenty years solvothermal reactions have been developed in different areas involving basic or applied researches. Several aspects can be considered:

- In Materials Chemistry: (i) the synthesis of novel materials, (ii) the development of nanochemistry,

- In Materials Science (i) the development of new crystal growth processes, (ii) thin film deposition, (iii) new sintering processes in mild conditions.

In all these domains solvothermal conditions induce an increase of the reactivity and consequently open both : a specific way to novel materials and the development of new processes either for preparing or shaping materials.

Introduction

Solvothermal reaction can be defined as a chemical reaction involving a solvent either in subcritical or in supercritical conditions [1].

Such a solvent acts as a chemical component of the reaction or a fluid phase able, through its physico-chemical properties, to modify the reaction .solvothermal reaction can be considered as the generic term used for all solvents, hydrothermal reaction is the qualifying term when the solvent is water.

Hydrothermal reactions were mainly used for oxides. The development of different solvents (H_2S, NH_3, C_6H_6…) has allowed to apply such chemical reactions for several classes of materials: sulfides, nitrides, carbides…

Different factors play an important role on solvothermal reaction:

- the chemical nature of the solvent,
- the physico-chemical properties of this solvent,
- the nature of the precursors,
- the experimental conditions.

I. Main parameters governing the Solvothermal reactions

Among the different parameters able to manage the chemical mechanisms of a solvothermal reaction ,it is possible to select:

→ the chemical parameters including the nature of the solvent and the precursors,

→ the thermodynamical parameters: pressure, temperature.

The choice of the solvent is closely dependent on the chemical composition of the resulting material and also on its physico-chemical properties able to modify the reaction mechanism.

(critical temperature T_c, thermal stability, ability to induce the formation of complexes….).

Considering the precursors, the selection is mainly governed by their interaction with the solvent, (dissolution, formation of complexes…) , their reactivity…

The thermodynamical parameters, pressure and temperature, are in the most cases optimized in order to obtain the mildest experimental conditions able to lead to the preparation of the final material or to get the appropriated shaping (nanocrystallites, single crystal, thin film…).

Schematically three main domains of applications for solvothermal reactions can be described: (i) the synthesis of novel materials, (ii) the development of new processes, (iii) the shaping of functional materials.

II. Solvothermal synthesis of novel materials

In Materials Chemistry , the main interest of solvothermal reactions is to help the stabilization of novel materials or novel structures [2]. In a first approach three main illustrations will be given: (i) the synthesis of new original compositions, (ii) the preparation of hybride materials at the frontier between organic and inorganic chemistry, (iii) the stabilization of new solids possessing openstructure.

II.1 Synthesis of new original compositions

In this domain two examples can be given.

II.1.1 The preparation through "geomimetism" of a new class of material: the phyllosiloxides.

The objective of this study was to prepare new layered structures derived from natural phyllosilicates with the mica-phlogopite-type structure.

In order to reach such objective it was necessary to replace hydroxyl groups (OH^-) for oxygen (O^{2-}) and in parallel to induce cationic substitutions on O_h or/and T_d sites of the mica-phlogopite-type structure [$Mg^{2+}_{Oh} \rightarrow Al^{3+}_{Oh}$, $Al^{3+}_{Td} \rightarrow Si^{4+}_{Td}$] (Figure).

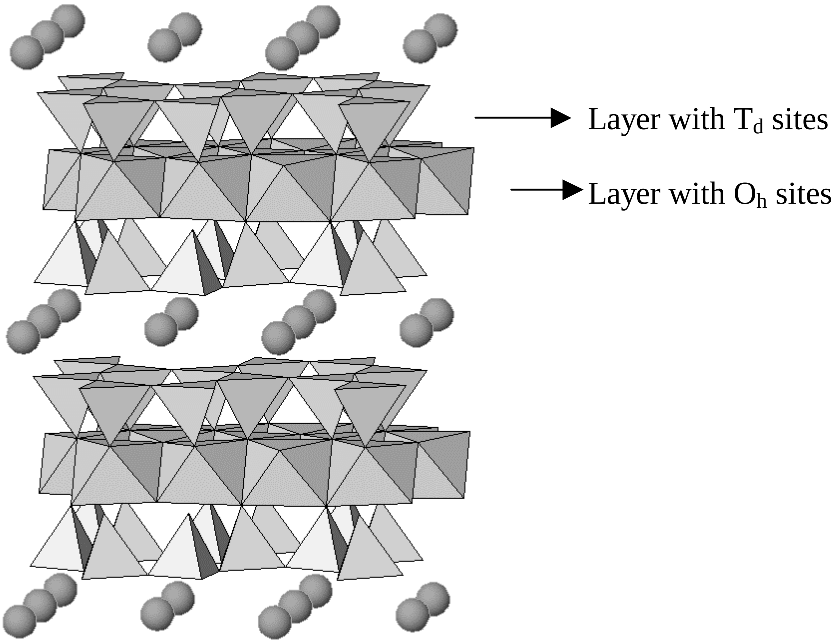

Figure : Schematic structure of a phyllosilicate with the mica-phlogopite type structure.

Using a two-steps process: a sol-gel step followed by a solvothermal treatment of the resulting aerogel as precursor and 2-methoxy-ethanol as solvent – a novel material with the composition $K(Mg_2Al)Si_4O_{12}$,derived from the mica phlogopite: $K(Mg_3)(Si_3Al)O_{10}(OH)_2$, was stabilized [3,4]. Then , such a matrix has been used for preparing new layered oxides with transition cations as Fe^{3+} or Fe^{2+} in the octahedral sites [5,6].

II.1.2 The preparation of carbonitrides

Since the theoretical prediction that the hardness of different C_3N_4 forms could be higher than that of diamond [7, 8] many research works have been developed for stabilizing such a composition.

Different approaches have been investigated: high pressure solid state synthesis [9], synthesis from organic precursors [10] and solvothermal reactions [11,12]. In such an approach the first tentative was the preparation of the graphitic form -as macroscopic sample -using $C_3N_3Cl_3$ as precursor and NH_2NH_2 as solvent ,in high pressure (3GPa) and medium temperature (800°C) conditions [13].

Then in order to reduce the preparation conditions different solvothermal reactions have been developed:

- Using 1, 3, 5 trichlorotriazine ($C_3N_3Cl_3$) and lithium nitride (Li_3N) as precursors with benzene as solvent, with experimental conditions :350°C, 5 MPa, the preparation of the β form of C_3N_4 was claimed [14].

- Using CCl_4 and NH_4Cl as precursors (in such a case an excess of the liquid phase CCl_4 can be used as solvent) in a temperature domain close to 400°C and with autogeneous pressure (few MPa) the formation of the graphitic form was announced [15].

II.2 The preparation of new organic-inorganic hybride materials

Due to their specific composition, the synthesis of such materials required mild conditions. At the beginning of the solvothermal processes, new mixed-metal carbonyl telluride clusters $[(Ph_4P)_2(Fe_2MTe_3(CO)_{11}]$ with M = Mo and W were prepared at 80°C and autogeneous pressure ,using $Fe_3(CO)_{12}$, $Mo(CO)_6$, Na_2Te_2 and Ph_4PBr as reagents and CH_3OH as solvent [16].

Thiogermanates $(enH)_4Ge_2S_6$ and $[M(en)_3]_2Ge_2S_6$ (M = Mn, Ni) with en=ethylenediamine were synthesized at 150°C and autogeneous pressure using GeO_2 and S_8 as reactants and ethylenediamine as solvent [17].

New organic-inorganic hybrid materials constructed from copper-organo-imine subunits and molybdoarsenate clusters have been recently described through hydrothermal reactions at medium temperature (180°) [18].

Solvothermal reactions have improved the development of such a class of materials [19].

II.3 The synthesis of materials with open framework

Inorganic open framework with regular pore architectures are an important class of functional materials because of their large domains of applications: catalysis, host-guest assemblies…

These structures are in many cases thermally unstable and consequently solvothermal processes in mild conditions appear a fruitful route.

Two illustrations can be given: the solvothermal synthesis of two new zinc phosphates $(C_8N_4H_{26})[Zn_2(HPO_4)_4]$ and $(C_8N_4H_{26})[Zn_6(PO_4)_4(HPO_4)_2]$ [20], the solvothermal synthesis of new mixed-valence iron alumino-phosphate $[Fe^{II}(H_2O)^2Fe^{III}_{0.8}Al_{1.2}(PO_4)_3]\ H_3O$ [21].

III. The development of new processes

The induction of new reaction mechanisms through the selection of appropriated precursors, solvent and thermodynamical conditions can lead to original processes for preparing functional materials. One of the most illustrative example is the synthesis of cubic boron nitride c-BN.

Due to the position of the elements B and N in the periodic table BN, isoelectronic of two carbons, presents the same structures that carbon (graphite-like (h-BN), zinc-blende (c-BN) and hexagonal lonsdaleite-type).

The elaboration process for c-BN is also based on a flux assisted conversion of h-BN using mainly nitrides as flux-precursors , such a process requires high pressures – high temperatures conditions [22]. During these last ten years different thermodynamical calculations [23] or experimental approaches (involving the c-BN→h-BN transformation [24]) suggested that c-BN could be thermodynamically stable in normal pressure conditions in mild temperatures conditions.

The first solvothermal process ,using a nitriding solvent (NH_2NH_2) as flux and h-BN as precursor,led to a strong reduction of the pressure – temperature conditions ($P=1.7$ GPa, $T\approx600°C$) compared to the conventional ones ($5<P<7$ GPa, $1000<T<1700°C$) [25].

During these last five years ,different solvothermal processes have been investigated at different temperatures, using boron halides (BCl_3, BBr_3) and nitrides (Li_3N) as precursors and an organic solvent (C_6H_6) [26-28]. A specific hydrothermal reaction called “phase selective process” has been also used with H_3BO_3 and NaN_3 as reagents and $N_2H_4.H_2O$ as solvent [29].

In some cases, the formation of c-BN was claimed, opening a new route to the synthesis of superhard materials.

IV. Solvothermal reactions and the shaping of functional materials

In order to improve the functionality of materials three different ways have been developed:

- the preparation of nanocrystallites,
- the elaboration of single crystals,
- the deposition of thin films.

During these last ten years solvothermal reactions have been developed in these different axis.

IV.1 Elaboration of small crystallites

Concerning the synthesis of well-defined nanocrystallites, in size and morphologies, solvothermal reactions – due to the wide spread of solvent composition – have allowed to developed borides [30], carbides [31], nitrides [32], phosphides [33], sulfides [34], selenides [35] (* *due to the large development of such research domain only some examples are quoted*).

IV.2 Crystal growth in solvothermal conditions

The main characteristic of these processes is the low or medium temperature used compared to the conventional processes.

The hydro- or solvothermal crystal growth is developed mainly in three directions:

- for obtaining single crystals with a low-temperature form [36],
- for preparing single crystals with a low density of defects (increasing temperature being able in many cases to favor it) [37,38],
- for developing new crystal-growth processes of non-oxides (nitrides, sulfides…) [39].

The main illustration concerning the first domain of application is the hydrothermal crystal growth of α-quartz [36]

In the near future the third domain of applications will be intensively developed using non-aqueous solvents. For example, recently the crystal growth of GaN using NH_3 as solvent and Li_3GaN_2 as precursor has been evaluated [40]. Single crystals of different materials as ZnS, PbS, SnS_2…– due to their physical properties – will be required for different applications leading to the development of new crystal-growth processes.

IV.3 Solvothermal deposition of thin films

Such a process has been tested in few cases: carbon deposition on SiC as substrate [41], chromium oxides on whiskers of aluminium borate [42].

Such processes require an evaluation versus the conventional ones (CVD, PVD) in order to be developed.

IV.4 Solvothermal sintering

Due to the reactions induced , under high pressure and medium temperature , between the solid and the fluid phases at the interface between the grains, hydrothermal sintering as been developed [43]. The main advantage of such a sintering process is to be efficient at medium temperature compared to the conventional sintering processes .Consequently this sintering process open a new route to the preparation of dense ceramics in mild conditions.

Conclusions

Solvothermal reactions appear a fruitful tool in different domains involving Materials Chemistry and Materials Science. Such reactions open the development of new processes either for preparing and shaping materials with different compositions (borides, nitrides, sulfides, selenides….). In the future ,such developments will be closely associated to different applications concerning in particular semi-conductors, optics, opto-electronic, spintronic…

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