NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Solvothermal reactions: an original route for the synthesis of novel materials

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Abstract Twenty years after the first development of solvothermal reactions, it appears important through the last research activities to trace the future trends taking into account their potentialities and the different economical constraints. During these last 20 years solvothermal reactions have been mainly used from preparing micro- or nanoparticles with different morphologies. Due to the importance to dispose of new materials for developing either basic research or industrial applications, such a presentation will be only focussed on the potentialities of solvothermal reactions in materials synthesis. Solvothermal reactions are mainly characterized by different chemical parameters (nature of the reagents and of the solvent) and thermodynamical parameters (in particular temperature, pressure). (a) The selection of the composition of the solvent opens new research areas for stabilizing materials belonging to different classes of materials (alloys, oxides, nitrides, sulphides…). (b) The mild temperature conditions generally used are able to improve chemical diffusion and reactivity in order to help the preparation of specific materials at the frontier between either different classes of inorganic materials (oxides-nitrides, nitrides-halides…) or inorganic/organic, inorganic/biologic frameworks. (c) The high pressure conditions, due to the small conveyed energy compared to temperature, allow also to stabilize metastable frontier materials (geo-inspired or bio-inspired materials). (d) In the future, taking into account, from one side: the economical and the environmental constraints, and from the other: the industrial demand of materials characterized by specific physical, chemical and biological properties, the potential developments of solvothermal processes will be analyzed.

Introduction

A solvothermal process can be defined as "*a chemical reaction in a closed system in the presence of a solvent (aqueous and non aqueous solution) at a temperature higher than that of the boiling point of such a solvent*". Consequently a solvothermal process involves high pressures. The selected temperature (sub- or supercritical domains) depends on the required reactions for obtaining the target-material through the involved process.

In the case of aqueous solutions as solvent, the hydrothermal technology have been studied and developed a long time ago with different objectives: (i) mineral extraction (as for leaching ores [1]), (ii) investigation of the synthesis of geological materials [2, 3], (iii) synthesis of novel materials [4–6], (iv) crystal growth—in particular the elaboration of α-quartz single crystals due to its piezo-electric properties [7], (v) the deposition of thin films [8], (vi) the development of sintering processes in mild conditions [9], (vii) the elaboration of fine particles well defined in size and morphology [10].

Hydrothermal processes—due in particular to the chemical composition of water as solvent—is mainly appropriated to the preparation of hydroxides, oxihydroxides or oxides versus the temperature value. The development of non-oxide materials (in particular nitrides, chalcogenides…) for investigating their physical properties and for industrial applications required the development of

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new processes involving non-aqueous solvents. Consequently, if solvothermal reactions is a "*generic term*" for a chemical reaction in a close system in presence of a solvent, these reactions are mainly developed with non-aqueous solvents for preparing non-oxide materials.

During these last 40 years hydrothermal reactions have been used in Materials Chemistry [5, 11] or Materials Science for developing soft processing in advanced inorganic materials [12] or for preparing functional ceramics [13, 14].

The interest for non-oxide materials has led to the development of solvothermal reactions either for preparing novel materials or for setting-up new processes leading to nanostructured materials [4, 15].

The interest of hydrothermal/solvothermal reactions in a large domain of applications (materials synthesis, crystal growth, thin films deposition, low temperature sintering…) has improved the development of new processes involving original technologies as hydrothermal-electrochemical methods [16], microwave-hydrothermal method [17].

Chemical reactions into a solvent (aqueous or non-aqueous) under high pressure and mild temperature conditions (sub- or supercritical domain of the selected solvent) appear promising for developing Materials Chemistry and Materials Sciences (in particular for nanotechnologies).

Main parameters governing solvothermal reactions

Two types of parameters are involved in solvothermal reactions:

→ the chemical parameters,
→ the thermodynamical parameters.

Table 1 gives the correlations between such parameters and the corresponding solvothermal reactions.

Chemical parameters

Two different parameters can be taken into account: the nature of the reagents and the nature of the solvent.

The chemical composition of the precursors must be appropriated to that of the target-materials. In addition, the concentration of the precursors seems to play a role on the control of the shape of nanocrystallites resulting of a solvothermal process. Wang et al. [18] through the solvothermal preparation of CdSe and CeTe nanocrystals have claimed the control of the crystallites-shape (dot, rod,…) with the concentration of the precursors. The interactions between reagents and solvent play an important role in the solvothermal reactions.
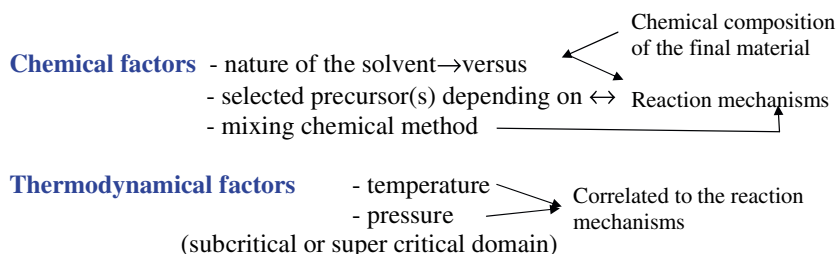
The selection of the solvent plays a key-role through the control of the chemical mechanisms leading to the target-material.

The reaction mechanisms induce, during the solvothermal reactions, are dependent on the physico-chemical properties of the solvent. For example Li et al. [19] have described the preparation of Cu_7Te_4 using $CuCl_2$, H_2O and tellurium as reagents and ethylenediamine as solvent. Using the same experimental conditions but changing only the nature of the solvent (benzene or diethylamine), tellurium did not react with copper chloride. Compare to non polar solvent as benzene, ethylenediamine is a polarizing solvent—such a property being able to increase the solubility of the reagents. In addition its complexing properties can play an important role in the reaction mechanisms.
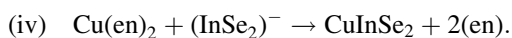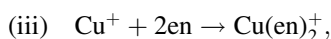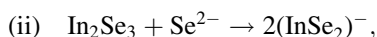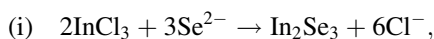
The complexing properties of the solvent can lead to the intermediate formation of stable complexes systems $(M(en)_3^{2+})$. Such a complex-cation can act as a template due to its octahedral geometry and can be incorporated into the structure of the final material. This type of solvothermal reactions has led to the synthesis of Sb(III) and Sb(V) thioantimonates $[Mn(en)_3]_2Sb_2S_5$ and $[Ni(en)_3(Hen)]SbS_4$ [20].

In some cases the formation of complex-cations is important as an intermediate step during the solvothermal reaction mechanisms. This is the case of the solvothermal preparation of the semiconductor material $CuInSe_2$ [21]. The starting products were $CuCl_2$, $InCl_3$ and Se. The solvent was either ethylenediamine (en) or diethylamine. The selected experimental conditions were 180 °C and the

Table 1 Main factors governing solvothermal processes

Chemical factors - nature of the solvent→versus ⟶ Chemical composition of the final material
  - selected precursor(s) depending on ↔ Reaction mechanisms
  - mixing chemical method ⟶

Thermodynamical factors - temperature ⟶ Correlated to the reaction mechanisms
  - pressure ⟶
  (subcritical or super critical domain)

resulting autogeneous pressure. The propose reaction mechanisms involve four steps:

(i) $2InCl_3 + 3Se^{2-} \rightarrow In_2Se_3 + 6Cl^-$,

(ii) $In_2Se_3 + Se^{2-} \rightarrow 2(InSe_2)^-$,

(iii) $Cu^+ + 2en \rightarrow Cu(en)_2^+$,

(iv) $Cu(en)_2 + (InSe_2)^- \rightarrow CuInSe_2 + 2(en)$.

The nucleophilic attack by amine could activate selenium to form Se^{2-} in a similar way that sulphur is activated by amine to S^{2-} [22, 23]. The formation of the $Cu(en)_2^+$ complex (Cu^+ resulting from the in situ reduction of Cu^{2+}) seems to play are important role in controlling the nucleation and growth of $CuInSe_2$ nano-whiskers. Replacing ethylenediamine by ethylamine as solvent, the reactivity is lowered and the resulting morphology consists on spherical particles of $CuInSe_2$. Consequently the nature of the solvent can act on the reactivity and the morphology of the resulting crystallites.

The physico-chemical properties of the selected solvent can also play an important role for orienting the structural form of the final material. Lu et al. [24] have underlined that the solvothermal synthesis of MnS can lead to metastable (β and γ) or stable (α) structural forms versus the composition of the solvent. Using $MnCl_2 \cdot 4H_2O$ and $SC(NH_2)_2$ as reagents and either an hydrothermal reaction (water as solvent) and or a solvothermal reaction (ethylenediamine as solvent), the stable form (α-MnS) with the rocksalt structure was observed. With the same reagents but with benzene as solvent, the wurtzite type structure (γ-MnS) was prepared, with tetrahydrofurane (THF) only the zinc-blende structure (β-MnS) can be observed.

The stabilization of different structural forms: stable α form or metastable forms (β, γ) versus water and the two others solvents (benzene and tetrahydrofurane) can be attributed to the ability to form a stable Mn complex ($Mn(H_2O)_6^{2+}$ or $Mn(en)_3^{2+}$) during the reaction mechanisms. The difference observe between benzene and THF suggests that a non polar solvent (C_6H_6) is more appropriated for stabilizing the wurtzite-form (γ-MnS). Consequently the solubility of the Mn^{2+} precursor appears to play also an important role for orienting the stabilization of a stable structural form.

Another example is the selective synthesis of $KTaO_3$ either as perovskite or pyrochlore structure versus the composition of the mixed solvents (water-ethanol or water-hexane systems) with a KOH concentration one order of magnitude lower than that in conventional processes [25].

The oxidation-reduction properties of the solvothermal medium during the reaction can be induced by the nature of the solvent or the composition of mixed solvents and by the use of additives.

The solvothermal processing of Sb(III)Sb(V)O$_4$ nanorods from Sb_2O_5 powder involves the reducing properties of ethylenediamine as solvent [26]. At the same temperature (200 °C), if the reaction time is one day only Sb(III)Sb(V)O$_4$ nanorods are formed but after 3 days only metallic Sb particles are observed.

The formation of copper (I) chloride particles with tetrapod-like-morphology used a mixture of acetylacetone and ethylene-glycol as solvent (50/50) and $CuCl_2 \cdot 2H_2O$ as precursor. During the solvothermal processing of such particles acetylacetone acts as reducing agent ($Cu^{2+} \rightarrow Cu^+$) whereas ethylene-glycol favourizes the anisotropic shape for CuCl crystallites [27].

On the contrary the solvothermal preparation of InAs as nanoscale semiconductor from $InCl_3$ and $AsCl_3$ as reagents and xylene as solvent requires the use of Zn metal particles as additive. The reaction mechanisms could be described as a co-reduction route: $In^{3+} \rightarrow In^0$ and $As^{3+} \rightarrow As^0$, through the reaction: $InCl_3 + AsCl_3 + 3Zn \rightarrow InAs + 3ZnCl_2$ [28].

Another interesting illustration of the use of reducing agent in addition of the reagents involves the preparation of the mixed-valent spinel $CuCr_2Se_4$, which is metallic and ferromagnet with a Curie temperature of 450 K [29]. Ramesha and Seshadri [30] have developed a solvothermal route for preparing this spinel using copper (II) acetylacetonate, chromium (III) acetylacetonate and Se powder as precursors. The additive was β-sitosterol (β-sitosterol through an aromatization process being able to transform Se powder to H_2Se).

Additive can be use also for orienting a specific morphology for the resulting crystallites. The preparation of the new-layered compound $Rb_2Hg_3Te_4$ through a solvothermal reaction can illustrate such a chemical route. The reagents Rb_2Te, Hg_2Cl_2 and Te are mixed into ethylenediamine as solvent. Oxido-reducing reactions are involved during the solvothermal process: $Hg_2^{2+} \rightarrow 2Hg^{2+} + 2e^-$ and $Te + 2e^- \rightarrow Te^{2-}$. Then the reaction, with the precursor Rb_2Te, leads to the synthesis of $Rb_2Hg_3Te_4$. The use of $FeCl_2$ as additive was found to be essential in the crystal growing process of $Rb_2Hg_3Te_4$ [31].

The thermodynamical parameters

These parameters are: temperature, pressure and the reaction time. The solvothermal reactions are mainly developed in mild temperature conditions : (T < 400 °C). Temperature and pressure improving in the major cases the solubility, the increase of such parameters induces an enhancement of the precursors-concentration into the

solvent and then favours the growing process (in particular in the preparation of micro- or nanocrystallites).

The brief analysis of the main factors governing solvo-thermal reactions underlines that the nature of the selected solvent plays a key-role, in particular for controlling the chemical mechanisms involved in the solvothermal reactions.

Development of solvothermal reactions

Reactions involved in solvothermal processes

Solvothermal reactions involve "in situ" different reaction-types as mentioned through the analysis of the chemical factors governing such processes. In particular, it is possible in a first approach to classify the reactions in approximately 5 types: (i) oxidation-reduction, (ii) hydrolysis, (iii) therm-olysis, (iv) complex-formation, (v) metathesis reactions.

The development of these different reactions implies to control carefully the chemistry in non-aqueous solvents and consequently to get more information's concerning the physico-chemical properties of such solvents.

Main applications of solvothermal processes

Solvothermal reactions have been developed in different scientific domains:

→ the synthesis of novel materials (design of materials with specific structures and properties),
→ the processing of functional materials (an emerging route in synthesis chemistry),
→ the crystal growth at low-temperature (a way to single crystals of low-temperature forms or with a low density of defects),
→ the preparation of micro- or nanocrystallites well define in size and morphology (as precursors of fine

structured ceramics, catalyst, elements of nano-devices…),
→ the low- temperature sintering (preparation of ceramics from metastable structural forms, low temper-ature forms or amorphous materials),
→ the thin films deposition (with the development of low-temperature processes)

Such a paper being devoted to the development of solvothermal reactions in Materials Chemistry a specific attention will be given to the synthesis of novel materials and the development of new processes.

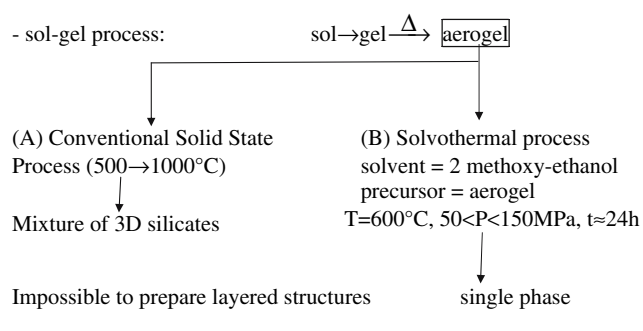## Solvothermal synthesis of novel materials

Roy has described the challenge for synthesizing new materials to specification [32]. Hydro- and solvothermal technologies being able to bring some new synthesis routes in mild conditions [33], such a synthesis routes appear promising for developing functional materials.

Geo-inspired materials

The structure of natural materials can be a source of inspi-ration for the conception of novel materials. Phyllosilicates is a large class of geomaterials characterized by layered structures. In most cases OH groups participate to such structures and consequently are a limitation of the thermal stability due to the reaction: $2OH^- \rightarrow H_2O_{vapor}^{\nearrow} + O^{2-} + \square$ (anionic vacancies). When the concentration of anionic vacancies increases the structure is decomposed. In order to impede such a phenomenon, the objective was to prepare a new class of layered oxides free of OH groups but always isostructural of the natural phyllosilicates. Due to the charge difference between OH^- and O^{2-} a cationic substitution must be initiated: $M^{2+} \rightarrow M^{3+}$ or $M^{3+} \rightarrow M^{4+}$ (in O_h and or T_d sites) (Fig. 1).

Fig. 1 Schematic structure and composition of a phyllosiloxide $(KMg_2AlSi_4O_{12})$ (**b**) through cationic substitutions in the mica-phlogopite lattice $(KMg_3AlSi_3O_{10}(OH)_2)$ (**a**)
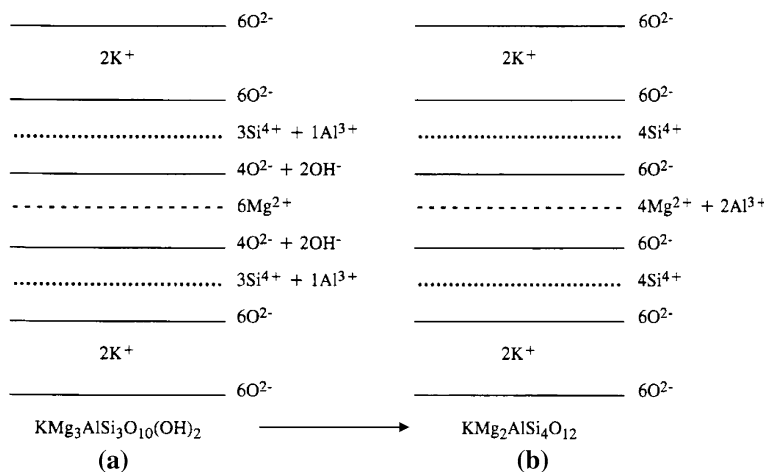
Table 2 Comparison of two preparation processes tested for stabilizing phyllosiloxides from a sol→gel starting step

- sol-gel process: sol→gel $\xrightarrow{\Delta}$ aerogel

(A) Conventional Solid State   (B) Solvothermal process
Process (500→1000°C)   solvent = 2 methoxy-ethanol
                                      precursor = aerogel
                                      T=600°C, 50<P<150MPa, t≈24h
Mixture of 3D silicates

Impossible to prepare layered structures   single phase

A two-steps process has been developed. The first consisted on a sol-gel process [using as precursors $Si(OC_2H_5)_4$, $Al(OC_4Hg)_3$, $Mg(OC_2H_5)_2$ and $KOCH_3$]. The second was a solvothermal treatment of the resulting gel ($50 < P < 100$ MPa, $650 < T < 750$ °C) using the 2-methoxy-ethanol as solvent (Table 2). The resulting material with the composition $K(Mg_2Al)Si_4O_{12}$ is isostructural to the mica-phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$. Such a new layered oxide (called phyllosiloxide) has been characterized through different techniques (XRD, TEM, RMN…) and has been tested as an interphase in ceramic-matrix composite (Fig. 2) [34, 35].

Solvothermal processes open the route to a novel class of bidimensional oxides derived from natural phyllosilicates.

Materials with light elements

Such a class of materials presents a strong interest, the strong chemical bonding inducing specific physico-chemical properties as hardnest, insulating, optical…. In the main cases the weak reactivity of the precursors requires for the synthesis severe pressure and temperature conditions.

Due to the enhancement of the reactivity observed for solvothermal reactions, during these last fifty years, such processes were investigated for preparing in particular: diamond, c-BN and C_3N_4.

Hydrothermal synthesis of diamond

Due to its large variety of physico-chemical properties, diamond has, during these last 50 years, required a great attention for developing new synthesis routes in mild temperature-pressure conditions.

The conventional route industrially developed for preparing diamond involved a flux-assisted conversion from graphite as reagent and a metallic flux as solvent Yamada et al. [36] have underlined the role of water in the "Mg_2SiO_4–graphite" system in the diamond formation under high temperatures-high pressures conditions. The flux-assisted conversion route using metallic systems as solvents requiring severe P, T conditions and being probably different than the natural process developed in the crust of the earth, many researchers have tried to reproduce the nucleation and the growth of natural diamonds. Different routes have been explored: (i) the decomposition of minerals [37], (ii) the investigation of different systems involving transition metal-carbon or carbide and water as Ni–NaOH–C, Ni–C–H_2O, SiC–H_2O [38–40], (iii) the hydrothermal decomposition of chlorinated hydrocarbon. Recently Korablov et al. reported that diamond structured carbon has been synthesized at 300 °C and 1 GPa using as reagents: 1, 1, 1-trichloroethane and 10 M NaOH solution as solvent in the presence of hydrogenated natural diamond or c-BN seeds [41]. In this hydrothermal approach the temperature and pressure conditions (140 MPa–800 °C) for diamond deposition appear a promising route. In addition diamond being metastable in such conditions, supercritical water under high pressures seems to play an important role. Such solvothermal processes must be re-investigated through the selection of reagents and solvents able to promote carbon diffusion and deposition.

Solvothermal preparation of cubic boron nitride (c-BN)

Cubic boron nitride, due to the position of B and N in the Periodic Table adopts the same structures than diamond. Cubic boron nitride was firstly prepared by Wentorf [42] through a flux assisted—conversion process using h-BN as precursor. During these last 20 years through different approaches (thermodynamical calculations, c-BN P, T stability…) several equilibrium curves (h-BN/c-BN) have been proposed by Solozhenko [43] and Maki et al. [44] (Fig. 3). The main characteristic of these curves is the intersection with the axis of temperature suggesting that c-BN could be thermodynamically stable at normal pressure conditions.

Two different approaches have been developed during these last 10 years in order to prepare, through a solvothermal process c-BN in mild pressure and temperature conditions: (a) the use of nitriding solvent for the flux-assisted conversion h-BN→c-BN, (b) the development of metathesis reactions and a non polar solvent. Through the first approach, hydrazine NH_2NH_2 has been developed as solvent for studying in such solvothermal conditions the h-BN→c-BN conversion in presence of Li_3N as additive [45]. Figure 4 gives a schematic view of the curves h-BN/c-BN underlining the synthesis P, T conditions of c-BN.

Fig. 2 Physico-chemical characterizations of the phyllosiloxide $K(Mg_2Al)Si_4O_{12}$
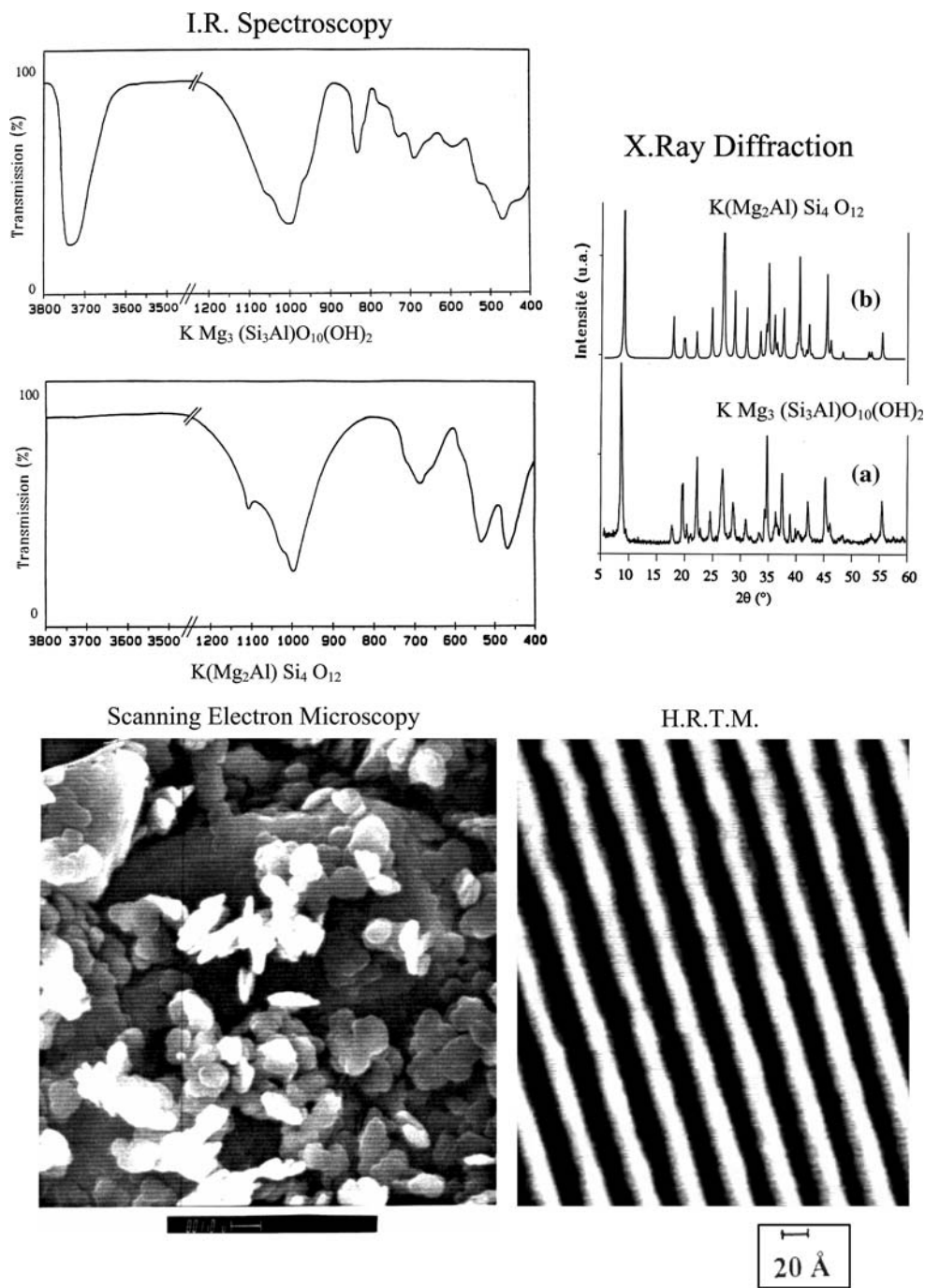

The mildest P, T conditions leading to the preparation of c-BN were 1.7 GPa and 500 °C.

During these last 5 years different solvothermal reactions have been investigated using benzene as solvent and a metathesis reaction between boron halogenides and a nitride. Using BBr_3 and Li_3N as reagents the influence of the temperature has been studied [46, 47]. At low temperature, h-BN is predominant and the c-BN formation is improved at increasing temperature (T < 480 °C, P = autogeneous pressure). The influence of the chemical composition of the boron chalcogenide has been also investigated [48]. In the same P, T conditions (autogeneous pressure, 250 °C) with Li_3N and benzene as solvent, h-BN is the dominant phase for BBr_3 as reagent and c-BN in the case of BCl_3. In parallel the influence of the induction effect (using nano-crystallites of GaP isostructural of c-BN as seeds and $BBr_3 + Li_3N$ as precursors and benzene as solvent with the same P, T conditions) has been underlined. The cubic phase is predominant whereas without such seeds only the h-BN formation is observed [49]. Different
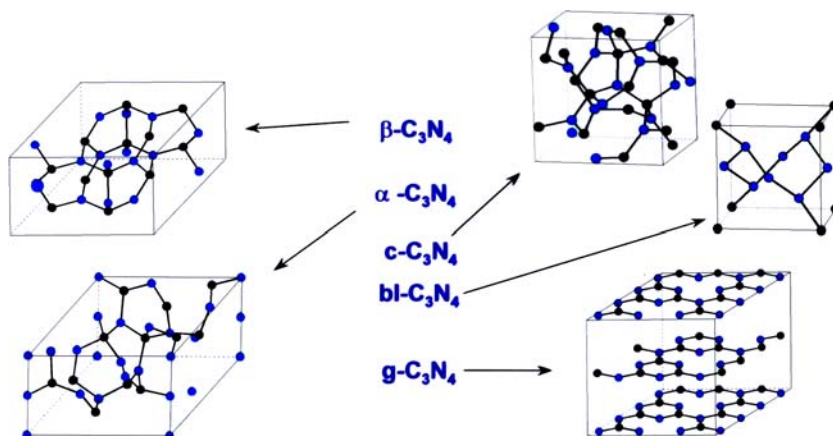
Fig. 3 Equilibrium c-BN/h-BN curves according to Maki et al. [44] and Solozhenko [43] compared to that derived from the diamond/graphite curve
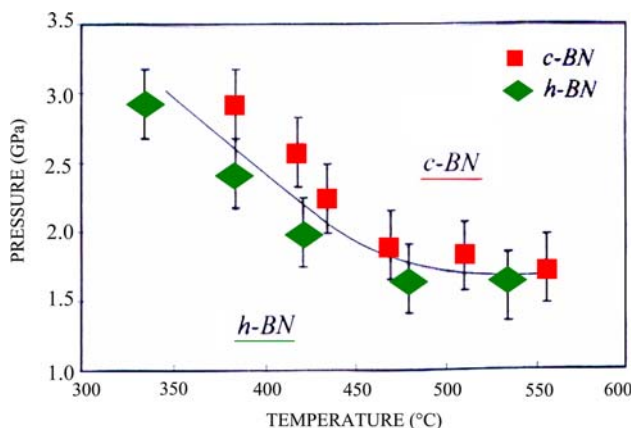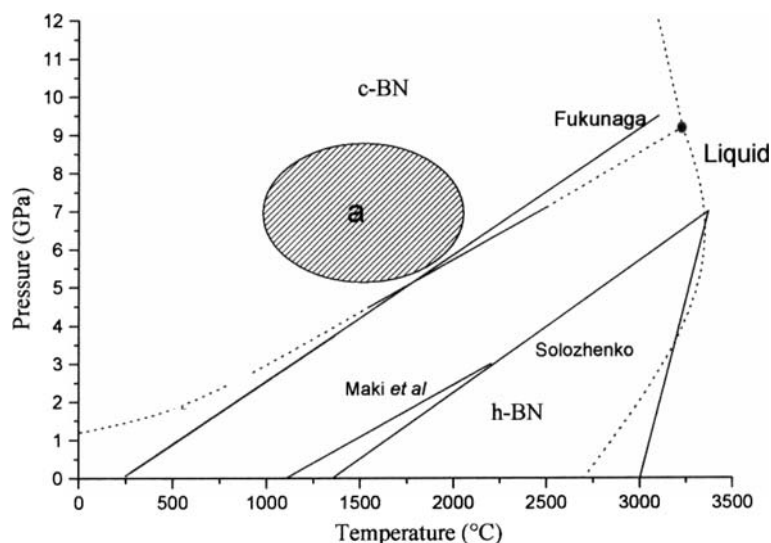
Fig. 4 H.P. domain concerning the c-BN synthesis using a solvo-thermal process (h-BN as reagent, NH_2NH_2 as solvent and Li_3N as additive) [45]

solvothermal processes has been tested with different nitride reagents as NaN_3 [50] or different solvents as aqueous solutions [51].

The c-BN synthesis through a solvothermal process appears an important challenge not only for improving the knowledge of its thermodynamical stability but also for industrial developments, c-BN being not only a superhard material but also the first III–V compounds able to improve applications in electronics and optoelectronics.

Solvothermal elaboration of C_3N_4

The prediction of the stability of carbon-nitride as C_3N_4 through ab-initio calculations [52] has largely improved a strong interest for such a material through different physico-chemical approaches (CVD, PVD, high pressures…). In addition through ab-initio calculations Teter and Hemley [53] have predicted five structural forms for C_3N_4. One derived from the 2D graphitic structure and four with 3D dimensional network (two derived from the α and β forms of Si_3N_4, one from the zinc-blende structure and a new-one isostructural of the high pressure form of Zn_2SiO_4) (Fig. 5).

Fig. 5 Prediction of different structural forms adopted by C_3N_4 [53]

Solvothermal reactions have been investigated for the C_3N_4 synthesis. The first consisted on the condensation of melamine (2-4-6-triamino-1-3-5 triazine) (1) and cyanuric chloride (2-4-6 trichloro-1-3-5 triazine) (2) in mild conditions (130 MPa, 250 °C) using triethylamine (Et_3N) as a weak nucleophilic solvent for trapping the by-product HCl [54]. The resulting material was the graphitic C_3N_4 form. A second route involving the thermolysis of melamine $C_3N_6H_6$ at high pressure (2.5–3 GPa) in the temperature range (800–850 °C) using NH_2NH_2 as solvent was investigated. In such a process g-C_3N_4 was obtained [55, 56].

More recently different solvothermal routes based on metathesis reactions have been investigated: (i) the reaction of CCl_4 and NH_4Cl at 400 °C and autogeneous pressure [57] leading to the graphitic C_3N_4, (ii) the liquid-solid reaction between anhydrous $C_3N_3Cl_3$ and Li_3N using benzene as solvent (355 °C, 5–6 MPa) where the formation of the α and β forms have been claimed [58].

A recent review paper gives an analysis of the potentialities of solvothermal reactions for preparing carbonitrides as bulk-material [59].

Solvothermal reactions appear a promising route to the synthesis of materials with light elements due to the strong interest of such materials for industrial applications. The improvement of the reactivity into supercritical solvents is able to lead to new industrial processes in mild temperature-pressure conditions.

Hybrid materials between inorganic and organic chemistry and stabilization of new structures

Due to the soft temperature conditions used for solvothermal reactions, it is possible to stabilize hybrid materials characterize by inorganic skeleton with the participation of organic molecules; the objective of such materials being to incorporate the functionality of both components. In the main cases, such hybrid materials are characterized by original open frameworks.

Among the different synthesis ways able to lead through solvothermal-reactions to hybrid-materials, two have been mainly investigated: (i) the use of specific templates, (ii) the biphasic solvothermal synthesis.

As an example the new one dimensional fluorinated nickel phosphate $Ni(HP_2O_7)F. C_2N_2H_{10}$ has been prepared solvothermally using ethylenediamine as the template [60].

The new copper adipate $[Cu(C_6H_8O_4)_3 (H_2O)_2 (C_6H_{11}OH)]$ was obtained using a biphasic solvothermal reaction [61]. Such a synthesis is based in the solubility difference of inorganic reagents and organic reagents in two different solvents (respectively: water and alcohol as 1-pentanol or cyclohexanol).

The designing and synthesizing of novel compounds with microporous structure are of important interest for their potential development in different fields: molecular sieves, ion-exchange, catalysis and separation [62–66].

Consequently solvothermal reactions were strongly developed for preparing novel hybrid materials with open framework. Different families of microporous structures have been prepared through a solvothermal process as—in particular: aluminophosphates [67–69], zinc phosphates [70, 71], organically intercalled oxides [72, 73] or chalcogeno-metallates [74–78].

Development of new processes for preparing functional nanocrystallites

During these last 15 years two important features have driven research activities:

– the investigation of non-oxide systems for potential physical properties,
– the development of nanotechnologies and the study of the correlations at this nanoscale between size-morphology and physical properties.

With the decrease of the crystallite size, sequential energy levels in semiconductors appears into discrete ones similar to those of molecules. This behaviour—called quantum confinement—induces a great change of their physico-chemical properties [79, 80] opening the route to new applications.

In addition during the past 15 years the research of specific nanostructures—in particular one-dimensional—as nanotubes [81–84], nanorods [85, 86] and nanowires [87–90] has been developed.

In parallel strong efforts have received considerable attention in order to understand the specific physical properties on such nanostructures in particular electronic [91], magnetic [92], optical [93].

The potentialities of solvothermal reactions for preparing nanostructures well characterized in size, morphology and architecture have been strongly investigated in different materials families as oxides halogenides, chalcogenides, nitrides, carbides, phosphides, metallics and intermetallics….

Considering nanostructured oxides, solvothermal processes were investigated for developing potential industrial applications. As examples it is possible to quote the preparation of barium titane powders for fine dielectric ceramics [94], TiO_2, α-Fe_2O_3 and $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) as pigment or catalyst [95–97], $Li_{1-x}Mn_2O_{4-y}$ or γ-LiV_2O_5 as electrode for lithium batteries [98, 99], $PbCrO_4$ and 1D manganese oxide for optical applications

[100, 101], ZnO due to its promising optical, electrical and piezoelectric properties [102].

Solvothermal reactions have been strongly developed for preparing nanostructured chalcogenides—in particular sulphides or tellurides—due to their large domain of applications (for example Cu_2SnS_3 [103], ZnS [104], $Fe_{1-x}S$ [105], $AInSe_2$ (A = Na, K) [106], CdS [107–109], NiS [110], SnS [111].

Different fluorides have been also synthesized as $KM^{2+}F_3$ with M = Mg, Zn [112] or M = Ni [113].

Nitride- in particular III–V materials as nanoparticles—have hold a strong interest due to the potential applications of such materials: InN [114], GaN [115], AlN [116]. Some others nitrides have been also investigated as CrN [117], VN [118], Cu_3N [119], ZrN [120].

Different nano-materials as Carbides: Mo_2C [121], B_4C [122, 123], phosphides: Co_2P, Ni_2P, Cu_3P [124] or TiP [125], boride: TiB_2 [126] have been also investigated using solvothermal processes.

Solvothermal synthesis of nanocrystallites with the nanotube-morphology have been developed during these last years -in particular carbon nanotubes [127–130], bismuth nanotubes [131], tellurium nanotubes [132] due to the potential applications of such specific morphology. In parallel intermetallic nano-particles as FePt nanowires have been investigated [133].

Solvothermal reactions appear also promising for the stabilization of novel molecular clusters [134].

Conclusion

Solvothermal reactions appear to be important for either the synthesis of novel materials, the preparation of nanostructured particles for nanotechnologies or the elaboration of bio-inspired materials for applications in Biosciences [135]. Due to the large variety of solvents or mixed-solvents able to be used and the different induced reactions-types versus the nature of the reagents and the chemical composition of the solvent, solvothermal processes will be important for developing original industrial processes in mild temperature and pressure conditions as for example the transformation of biomass as a renewable organic resource [136]. Nevertheless such a development will require an improvement of the knowledge of the physico-chemical properties of non-aqueous solvents under pressure and temperature conditions.

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