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Solvothermal processes: a route to the stabilization of new materials†

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Solvothermal processes are a powerful route for preparing materials. Different examples are given, either in water as solvent or in non-aqueous solvents such as alcohols, liquid NH_3 and NH_2NH_2. This quite new approach for materials synthesis will probably be strongly developed in the near future provided that the role of solvents in the supercritical conditions can be better understood from the chemical reactivity point of view.

Solvothermal processes can be defined as chemical reactions or transformations in a solvent under supercritical conditions or near such a pressure–temperature domain. The specific physico-chemical properties of solvents in these conditions can, in particular, markedly improve the diffusion of chemical species.

These processes have been mainly developed in the following scientific areas: (i) the synthesis of new materials, (ii) the development of new processes for preparing functional materials, and (iii) the shaping of materials (crystal growth or the preparation of fine microcrystallites).

The purpose of this paper is to present the potentialities of solvothermal processes for the preparation of original materials. To achieve this objective the main requirements are the optimization of the precursors and the nature of the solvent used.

Significant examples are reported in this paper in order to introduce the interest and the potentialities of the solvothermal reactions for preparing new materials. Furthermore this method is clearly highlighted with the recent preparation of the graphitic form of the carbon nitride C_3N_4.

1. Preparation of new materials through solvothermal reactions

The chemical composition of the solvent must be adapted to the material to be prepared, consequently the presentation of the different examples discussed in this paper will be correlated to this requirement.

1.1. Synthesis using water as solvent

1.1.1. Hydrothermal synthesis of new hydrated oxides. Hydrothermal chemistry has been extensively developed for the synthesis of advanced inorganic materials which are difficult to obtain by high temperature solid state reactions. In particular, hydrated materials are mainly prepared through processes involving such chemistry, the reactivity being increased under high pressure conditions and at moderate temperatures.

The preparation of compounds such as $A_xV_6O_{16}\cdot nH_2O$ (A = K, Rb, Cs, NH_4, Ca, Sr, Ba) with layered structures has been studied by Oka *et al.*[1] Several hydrated vanadium(IV,V) oxides with layered structures, also found in natural minerals, have recently been reviewed by Evans and Hughes.[2,3] The structures of such $A_xV_yO_z\cdot nH_2O$ compounds are built from V_yO_z layers of V—O polyhedral frameworks with A cations and water molecules placed in the interlayer domain. The frameworks of the V_yO_z layers exhibit different structural types according to their compositions: V_2O_5, V_2O_6, V_3O_8, V_4O_{11}, *etc.* The most developed preparation routes involve solid state reactions at high temperatures and consequently lead to anhydrous compounds. In this solvothermal synthesis the precursors were $VO(OH)_2$ and V_2O_5. Vanadium oxyhydroxide $VO(OH)_2$ was obtained by the hydrothermal treatment of $VOSO_4$ in NaOH solution at 150 °C for 24 h. To prepare $A_xV_6O_{16}\cdot nH_2O$ oxides, a suspension of $VO(OH)_2$ and/or V_2O_5 powders was treated under autogenous pressure at 250–280 °C for 24–48 h in aqueous solutions of alkali metal or alkaline earth salts (0.1–0.2 M). All the resulting compounds $A_xV_6O_{16}\cdot nH_2O$ (A = K, Rb, Cs, NH_4, $x = 2$, $n = 1.4$–1.6) are characterized relative to the natural mineral hewettite $CaV_2O_{16}\cdot 9H_2O$. This structure consists of V_3O_8 layers and interstitial Ca and H_2O species.

1.1.2. Preparation of anhydrous oxides. Anhydrous oxides can also be obtained through hydrothermal processes, the main factors able to orientate the formation of anhydrous materials being the nature of the starting materials and solvent, the concentration of the precursors, and in particular the temperature range used during the synthesis. The main advantage of the solvothermal process is to induce the preparation of metastable phases or to reduce considerably the reaction temperature and consequently the sintering effects.

Three examples can be given to illustrate the potential utility of the solvothermal method: (i) the hydrothermal synthesis of lithium manganese oxides with the spinel structure,[4] or $La_{0.50}Ba_{0.50}MnO_3$[5] where the concentration effect of the precursors appears a key factor, (ii) the formation of perovskite type oxides such as $Pb(Mg_{1/3}Nb_{2/3})O_3$[6] illustrating the effect of temperature on the structural form stabilized, and (iii) the preparation of silicates such as $Y_2Si_2O_7$,[7] underlining the role of the kinetics under such conditions.

The preparation of lithium and sodium manganese oxides involves the hydrothermal treatment of δ-MnO_2 with LiOH aqueous solution. While a spinel structure is observed for the lowest LiOH concentrations (*ca.* 0.4 M), a monoclinic phase Li_2MnO_3 is formed for the highest (*ca.* 1 M). In the spinel structure Mn ions and Mn vacancies are situated on the 16d octahedral sites and Li^+ ions on 8a tetrahedral ones.

The preparation of manganese oxides with the perovskite structure can involve solid state reactions at high temperatures[8,9] and sol–gel processes.[10]

The mixed valence manganese oxide $La_{0.50}Ba_{0.50}MnO_3$ which exhibits giant magnetoresistance has been prepared

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through a hydrothermal method from $KMnO_4$, $MnSO_4$, $La(NO_3)_3$ and $Ba(OH)_2$ in aqueous solution. The alkalinity and molar ratio of Mn(VII)/Mn(II) in the initial reaction mixture, associated with the hydrothermal reaction temperature, govern the crystallization of the resulting $La_{0.50}Ba_{0.50}MnO_3$ material.

The hydrothermal preparation of $Pb(Mg_{1/3}Nb_{2/3})O_3$ from aqueous solutions of lead and magnesium nitrates and an ethanolic solution of $NbCl_5$ leads to the pyrochlore or the perovskite structure depending on the temperature: the pyrochlore structure is observed at temperatures lower than 600 °C, the perovskite structure is formed above 600 °C.

Through solid state reactions the formation of $Y_2Si_2O_7$ requires high temperatures ($900 < T < 1800$ °C).[11] Through hydrothermal processes the chemicals used were yttrium acetate and tetraethylorthosilicate. The reaction time is directly correlated to the temperature: 100 days are required at 300 °C whereas 11 days are necessary at 600 °C.

Hydrothermal syntheses of oxides and fluorides have also been developed recently by Feng *et al.*[12] (Table 1).

1.1.3. Diamond crystal growth under hydrothermal conditions: a challenge? During the last ten years several works have been focused on the role of supercritical water on diamond formation. Yamada *et al.* have underlined the role of water in the Mg_2SiO_4–graphite system in diamond formation under high pressure and high temperature conditions (7.7 GPa, 1900 °C).[13] Without water, no diamond formation is detected, while in the presence of water a large number of diamond micro-crystals with octahedral shape are observed.

Many research works have attempted to reproduce, at moderate pressures and temperatures, the crystal growth of natural diamond (the nucleation requiring more energetic conditions). Different research groups have tried to grow diamond from the decomposition of minerals[14] or from different systems such as Ni–NaOH–C,[15] $SiC–H_2O$,[16] or more recently in the system $Ni–C–H_2O$.[17] In this hydrothermal approach to diamond deposition, the pressure and temperature conditions are relatively low (140 MPa, 800 °C) by comparison with those used for industrial diamond synthesis ($P \geqslant 5$ GPa, $T \geqslant 1200$ °C). Owing to the fact that diamond is metastable under these P,T conditions, water in supercritical conditions seems to play a specific role.

The crystal growth of diamond involving hydrothermal conditions can be compared to the deposition of diamond as thin films using CVD processes. In the CVD route the kinetics of diamond formation play an important role due to the small energy difference between the graphitic and the diamond forms of carbon. A critical analysis of solvothermal diamond deposition indicates that the improvement of the diffusion of carbon species in a solvent under supercritical conditions could play a key role in such a process. This deposition process must be more deeply studied in order to approach a better understanding of diamond deposition in the liquid phase in its metastable P,T domain of stability.

Table 1 List of hydrothermally synthesized complex oxides and fluorides

Compound	Hydrothermal reaction temp./°C	Time/days
$Na_xLa_{2/3-x/3}TiO_3$	240	7
$Na_xAg_yLa_{2/3-(x+y)/3}TiO_3$	240	7
$Na_xLi_yLa_{2/3-(x+y)/3}TiO_3$	240	7
$La_{1-x}Ca_xMnO_3$	240	3
$La_{1-x}Sr_xMnO_3$	240	6
$La_{1-x}Ba_xMnO_3$	240	3
$NaNdTi_2O_6$	240	3
$NaCeTi_2O_6$	240	3
$CaMo(W)O_4$	240	3
$SrMo(W)O_4$	240	3
$BaMo(W)O_4$	240	3
$LiBaF_3$	140	5
$KMgF_3$	120	8
$LiYF_4$	220	3
KYF_4	220	3
$BaBeF_4$	220	3
BaY_2F_8	240	3
$LiYF_4{:}Re^{3+}$	240	3
$BaY_2F_8{:}Re^{3+}$	240	3

1.1.4. Solvothermal preparation of carbon films under hydrothermal conditions. Carbon films can be used in a large range of applications from microelectronics to materials science.[18] Chemical vapour deposition (CVD) is mainly used for preparing carbon coatings but such a process is expensive and not well adapted for a large variety of substrates due to the temperature range required.

Hydrothermal treatment of SiC fibers (100 MPa, $300 < T < 600$ °C for 25 h) leads to the formation of a carbon film on the fiber surface. Such a phenomenon can be explained through the following equation:

$$SiC + 2H_2O \rightarrow C + 2H_2 + \text{‘}SiO_2\text{’}$$

Several investigations with different carbides indicate that such a chemical reaction occurs.[19] This hydrolysis of carbides at moderate temperatures could involve a new carbon chemistry near the surface of the involved substrates.

2. Solvothermal preparation of new materials using non-aqueous solvents

Although water or aqueous solutions were largely used as solvents in most solvothermal reactions, during the last few years several non-aqueous solvents have been investigated for the preparation of different materials. Two recent studies carried out in our Institute will be described, one involving the synthesis of phyllosilicate-like oxides without OH groups and the second showing that solvothermal synthesis using nitriding solvents can open a new route for the preparation of nitrides or to the stabilization of new nitrided materials.

2.1. Stabilization of a new class of bidimensional oxides: the ‘phyllosiloxides’

In order to improve the thermal stability of bidimensional structures derived from phyllosilicates, new oxide compositions have been designed on the basis of anionic ($OH^- \rightarrow O^{2-}$) and cationic ($M^{2+} \rightarrow M^{3+}$) coupled substitutions.

Using the mica phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$ as a model, a new composition, $K(Mg_2Al)Si_4O_{12}$, has been proposed (Fig. 1). Because of the complicated composition, a sol–gel process was developed to enable the use of a

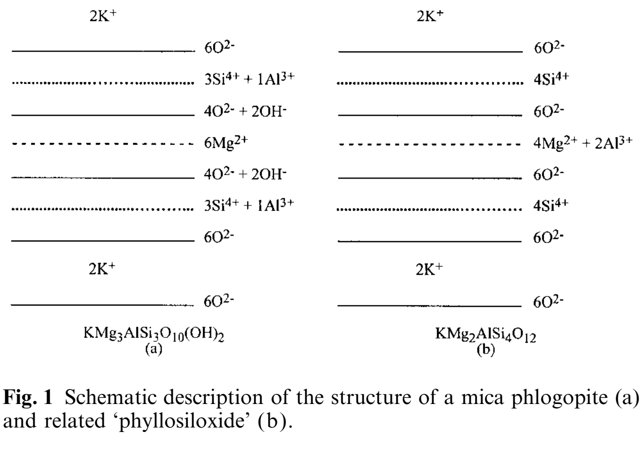

Fig. 1 Schematic description of the structure of a mica phlogopite (a) and related ‘phyllosiloxide’ (b).

homogeneous precursor. A gel was firstly prepared from the starting material $Si(OC_2H_5)_4$, $Al(OC_4H_9)_3$, $Mg(OC_2H_5)_2$ and $KOCH_3$. By using the conventional solid state treatment of such a gel at different temperatures in the range 700–1200 °C, only the formation of 3D silicates ($MgSiO_3$, Mg_2SiO_4, $AlSiO_5$) is observed.[20] Since such a thermal treatment at normal pressure did not lead to the formation of a layered structure isotypic with the mica phlogopite, a solvothermal treatment using 2-methoxyethanol as solvent (critical parameters T_c and P_c being: $4.7 < P_c < 4.9$ MPa, $277 < T_c < 297$ °C) was used. The optimized experimental conditions leading to a unique phase were: $50 < P < 100$ MPa, $700 < T < 800$ °C, $48 < t < 72$ h. The XRD pattern of this phase is isotypic with that of the micaphlogopite (Fig. 2). Physico-chemical characterization (TEM, IR and NMR spectroscopy) confirms the bidimensional structure of this new oxide, the absence of OH groups and the cationic distribution between O_h and T_d sites, in agreement with the structure of the mica phlogopite. TGA and XRD studies show an increase of the thermal stability (900–950 °C *vs.* 500–700 °C for the mica phlogopite parent structure).[21]

Such a 2D phyllosiloxide, $K(Mg_2Al)Si_4O_{12}$, has been tested as an interphase in ceramic–matrix composites.[22,23]

In such a case, the use of a solvent under supercritical conditions seems to orientate the formation of a unique phase instead of a mixture of silicates. In addition, the *in situ* stabilization of specific chemical species such as shaping agents could orientate a bidimensional structure through a synthesis route comparable to that used for preparing zeolites.

In order to obtain more information concerning the process *in situ* physical characterization such as for example infrared spectroscopy is necessary.

2.2. Preparation of nitrides using solvothermal processes in nitriding solvents (NH_3 or NH_2NH_2)

Different applications of solvothermal synthesis of nitrides can be developed: (i) to decrease the temperature of synthesis, (ii) to set up new processes in order to improve specific properties for the resulting material through shaping effects (*e.g.* monodispersed nano-sized particles), in particular for catalytic applications or ceramic precursors, and (ii) to prepare new metastable compounds.

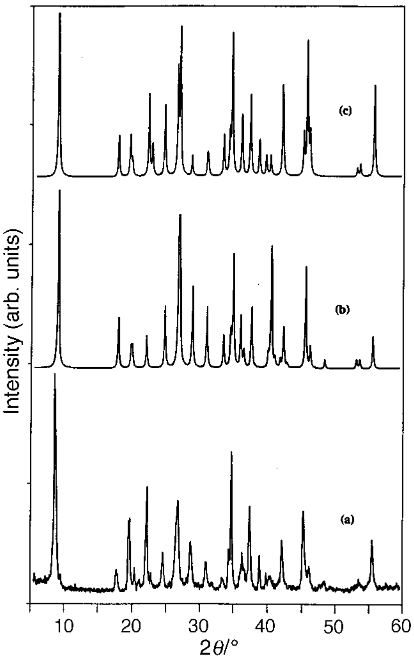

Fig. 2 XRD patterns (Cu-Kα) of: (a) $KMg_2AlSi_4O_{12}$ 'phyllosiloxide', (b) 1 M $KMg_3(Si_3Al)O_{10}(OH)_2$ phlogopite, (c) 2 M $KMg_3(Si_3Al)O_{10}(OH)_2$ phlogopite.

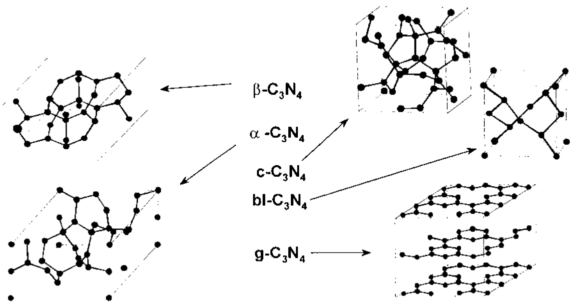

Fig. 3 The different possible structures claimed for C_3N_4.

2.2.1. Solvothermal process for preparing molybdenum nitrides as fine particles. In order to obtain molybdenum nitrides (Mo_2N and/or MoN) free of oxygen and as finely divided particles, the solvothermal reaction has been developed. By using precursors such as molybdenum oxides, the formation of oxynitrides as final product cannot be avoided. By using a precursor free of oxygen such as $MoCl_5$ and a nitriding solvent such as liquid NH_3 or NH_2NH_2, Mo_2N and MoN nitrides were obtained as crystallites characterized by BET isotherms, TEM and SEM.[24] Such finely divided molybdenum nitrides, free of oxygen and well controlled in shape, may open a new processing route to new catalysts.

2.2.2. Solvothermal preparation of a new nitride: C_3N_4 with the graphitic structure. The prediction of the stability of hypothetical solids through *ab initio* or 'first principle' calculations appears as a new challenge in solid state chemistry.[25]

The 3D materials containing light 2p elements such as B, C, N, O have received much interest from the scientific community due to the exceptional properties of the first members of this family, *e.g.* diamond or c-BN.[26–28] The compound C_3N_4 can be considered as an interesting member of this family due to the high value for the calculated bulk modulus of the β form ($B_{calc.} \approx 430$ GPa) isostructural with β-Si_3N_4, which is comparable to that observed for diamond ($B_{obs.} \approx 442$ GPa).[29–31] During the past 10 years five different structural types have been predicted through different *ab initio* calculations: one with the bidimensional graphitic structure (g-C_3N_4) and four with a three-dimensional lattice (β and α structures isotypic with that of Si_3N_4, one of the blende type with carbon vacancies and the last derived from the high pressure form of Zn_2SiO_4)[32] (Fig. 3).

Different attempts to prepare C_3N_4 either by CVD or PVD techniques or by high pressure routes would have led, in a few cases, to the formation of C_3N_4 microcrystallites corresponding to the different structural forms embedded in a large amount of an amorphous phase.[33,34]

We have used the same strategy as that developed for the synthesis of diamond c-BN through the flux assisted conversion process.[35] The preparation of the graphitic form of C_3N_4 as a macroscopic sample appears to be an important challenge to gain access to the 3D structural varieties.

In order to prepare such a graphitic form two different routes were investigated, both involving solvothermal reactions in non-aqueous solvents. The first consisted of the condensation of

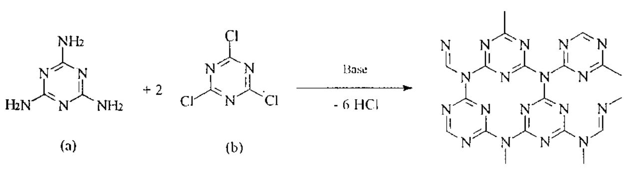

Fig. 4 Condensation of melamine on cyanuric chloride at medium pressure (130 MPa) and medium temperature (250 °C) using triethylamine as a weak nucleophilic solvent.

melamine (2.4.6-triamino-1.3.5-triazine) (a) and cyanuric chloride (2.4.6-trichloro-1.3.5-triazine) (b) at moderate pressure (130 MPa) and temperature (250 °C) using triethylamine (Et_3N) as a weak nucleophilic solvent in order to trap the resulting HCl formed during the reaction (Fig. 4). The second was the thermolysis of melamine $C_3N_6H_6$ at high pressure (2.5–3 GPa) in the temperature range 800–850 °C using hydrazine NH_2NH_2 as the nitriding solvent. In both cases the XRD analysis of the resulting material after the elimination of the unreacted and secondary products confirms the formation of a graphitic-type phase. The chemical analysis is in agreement with the composition C_3N_4. The first route involves the production of a large amount of hydrogen compared to the second one.

The physical characterization (FTIR spectroscopy, TGA and XPS analysis) of the material formed from the thermolysis of melamine under solvothermal conditions confirms the formation of g-C_3N_4.[35] It is worthwhile noticing that the high pressure and high temperature decomposition of melamine, involving the same experimental P,T conditions (2.5–3 GPa; 800 °C) as those used for the second route (above) but in the absence of the nitriding solvent NH_2NH_2, leads to the formation of only carbon graphite. Such a result underlines the chemical role of the solvent under supercritical conditions for stabilizing the C_3N_4 composition.

Different hypotheses can explain the stabilization of carbon nitride in the presence of NH_2NH_2 under supercritical conditions. (i) Owing to the stability of N_2, an average pressure of 3 GPa is not sufficient for stabilizing C_3N_4 at the temperature required for the thermal decomposition of $C_3N_6H_6$ and consequently NH_2NH_2 acts as nitriding solvent. In this case, the synthesis is governed by chemical effects. (ii) The high pressure thermal decomposition of $C_3N_6H_6$ leads to carbon nitride formation only if a solvent under supercritical conditions can help (through the high value of the diffusion of chemical species) the building of the graphitic variety. Consequently, kinetic effects could play an important role.

However, the narrow P,T domain for preparing C_3N_4 suggests that the kinetics effects could be predominant.

3. Conclusion

Solvothermal processes open a fruitful route for improving the synthesis of well known materials such as for example diamond, oxides and nitrides at temperatures and pressures much lower than those used in classical solid state chemistry methods. Furthermore the chemical reactions carried out in supercritical fluid media with appropriate precursors and solvents allow either the preparation of materials which are difficult or impossible to obtain by the ceramic route (*e.g.* phyllosiloxides) or the synthesis of metastable phases (*e.g.* C_3N_4 with graphitic structure). Another feature of the synthesis carried out under (near) supercritical conditions concerns the morphology of the materials which can be governed by varying three main parameters (pressure, temperature and reaction time). However for controlling the chemical reaction in order to obtain materials with specific composition, structure, morphology and properties it is absolutely necessary to understand more fully the chemical reactivity of supercritical fluids. This purpose requires the evolution of the chemical reaction to be followed *in situ* with the help of different spectroscopic observations. Such efforts are currently being made in this direction in our Institute.

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