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Solvothermal processes and the synthesis of nitrides

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Nitrides constitute an important class of materials due to their physical properties. In this way, all processes related to their synthesis or shaping are of relevant interest. A solvothermal process can be described as a reaction between precursors in a close system in the presence of a solvent and at a temperature higher than the boiling point of the solvent, with pressure being consequently involved. Depending on the pressure and temperature, the solvent is in sub- or supercritical conditions. The system precursors/solvent can be either homogeneous or heterogeneous. Concerning nitrides, solvothermal processes have been mainly developed in three domains:

- (1) the preparation of novel compositions,
- (2) the elaboration of nanocrystallites well defined in size and morphology,
- (3) the crystal-growth of functional nitrides such as GaN.

Considering the synthesis of novel nitrides, different solvothermal reactions can be used versus the nitriding agent (N^{3-} or N_3^-) and the nature of the solvent (nitriding solvent or non-reactive solvent). Different examples will be given and the potentialities of solvothermal processes in the preparation of novel nitrides will be discussed.

Keywords: solvothermal processes; nitrides; synthesis; nanocrystallites; crystal growth; solvothermal c-BN preparation

1. Introduction

Solvothermal processes are characterized by the reaction between precursors or the decomposition of a precursor in presence of a solvent in mild temperature and pressure conditions (the temperature being higher than the boiling point of the solvent). The solvent can be in sub- or supercritical condition and the system can be homogeneous or heterogeneous.

Solvothermal reactions were mainly developed in aqueous solutions (hydrothermal processes) for developing oxides. During the last 15 years, the interest for non-oxides (nitrides, phosphides, selenides, etc.) due to their physical properties [1,2] has led to use non-aqueous solvents and specific chemical reactions.

This article is devoted to the impact of solvothermal processes for developing nitrides, implying applications such as the synthesis of novel nitrides, the preparation of nanocrystallites, the crystal

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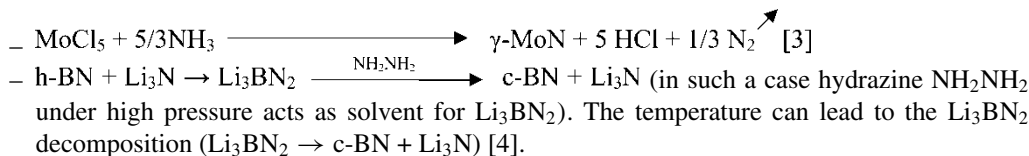
growth of single crystals, and the set-up of new processes in mild conditions for developing functional nitrides.

2. The principle of a solvothermal nitriding reaction

Due to the principle of a solvothermal process, the nitriding reaction can be induced either by the solvent or by the precursors (or, in some cases, additives).

The first route for solvothermal nitridation is the use of a nitriding solvent such as liquid NH_3 or liquid NH_2NH_2 .

Two examples can illustrate such a nitriding route.



The second route consists of using nitriding species. Here, three main types of nitriding reagents have been investigated: N^{3-} (as Li_3N) [5], N_3^- (as NaN_3) [6], and different nitriding molecules such as HMDS (1,1,1,3,3,3 hexamethyldisilazane) [7], ammonium dicyanamide ($\text{NH}_4 [\text{N}(\text{CN})_2]$) [8], amide (as LiNH_2) [9], etc.

3. Solvothermal synthesis of carbonitrides

During the last 15 years, the synthesis of carbonitrides (in particular C_3N_4) has been an important challenge [10].

Through *ab-initio* calculations different structural forms of C_3N_4 were postulated (Figure 1).

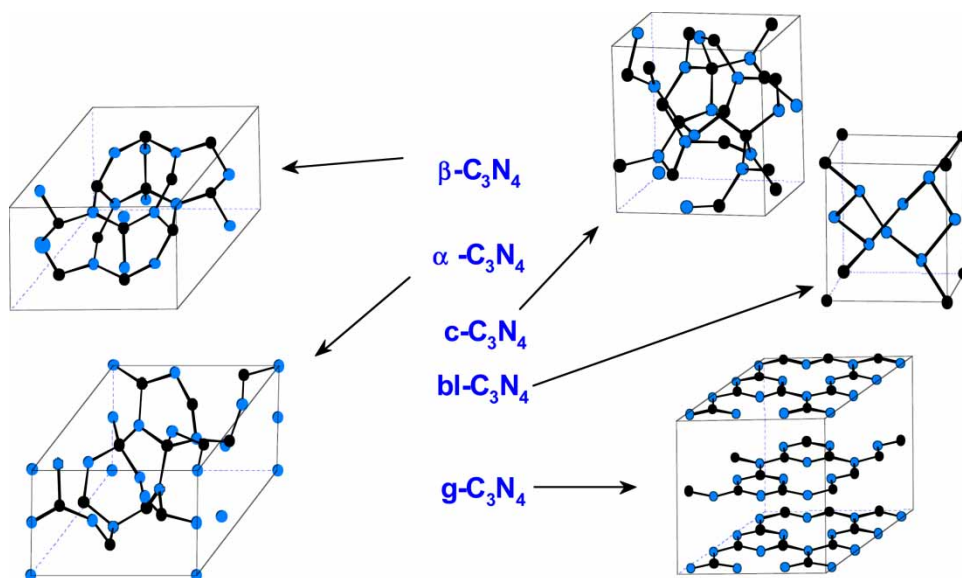


Figure 1. Structural forms of C_3N_4 proposed by Teter and Hemley [11].

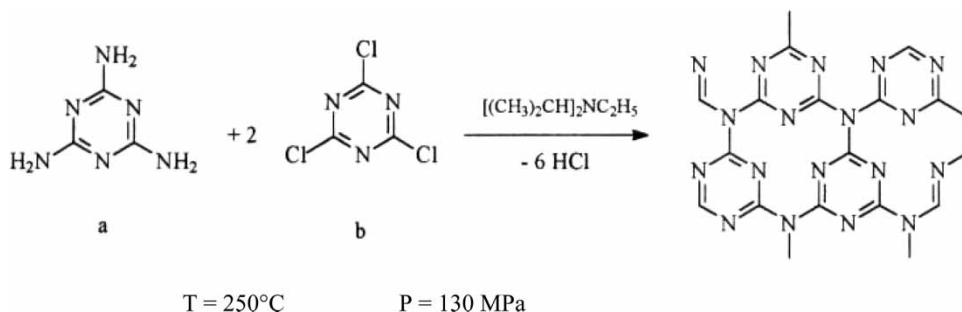


Figure 2. Solvothermal condensation of melamine and cyanuric chloride on presence of di-isopropyl-ethylamine as solvent [12].

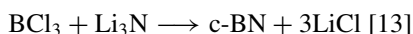
One of the first attempts for preparing the C_3N_4 graphitic form was investigated by Montigaud et al. [12]. The precursors were selected as melamine and cyanuric chloride, due to the existence of (C_3N_3) heterocycles. The solvent was di-isopropyl-ethylamine. The schematic solvothermal reaction for preparing g- C_3N_4 is given in Figure 2.

Several solvothermal reactions have been developed for preparing C_3N_4 using different precursors [10].

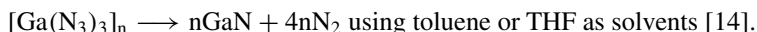
4. Solvothermal preparation of nitrides-nanocrystallites

Because pressure is a key parameter to govern the solubility of precursors, solvothermal processes are particularly adapted to control the nucleation and then the nanocrystal growth of small particles.

Different precursors, such as Li_3N and NaN_3 , have been developed as nitriding agents.



In some cases the solvothermal decomposition of metal azides can be used as precursors for preparing the corresponding nitride:



5. Solvothermal crystal growth of nitrides

During the last 10 years, gallium nitride has been selected due to its physical properties (wide-band gap semiconductor ($\Delta E = 3.42 \text{ eV}$ at 300 K), high electron mobility ($\mu = 5300 \text{ cm}^2\text{V.s.}$), saturation velocity ($v \leq 19 - 10^6 \text{ cm.s}^{-1}$), breakdown voltage ($V_{\text{BR}} = 26 - 33.10^6 \text{ cm.s}^{-1}$) [15]). Due to these properties, GaN can play a crucial role in opto-electronics, high frequency-high power electronics, and fast speed communication [16].

Due to the large experience issued from the crystal growth of α -quartz, the solvothermal crystal growth process appears a fruitful route for preparing GaN single crystals [16] compared with other methods, such as the hydride vapor-phase epitaxy (HVPE) [17], the high-pressure nitrogen solution growth [18], or the solution growth from Na flux [19].

A review of state-of-the-art GaN crystal growth underlines the recent progress during the last 15 years [20].

Two different types of solutions have been investigated: (i) NH_3 with basic mineralizers, such as NaNH_2 and KNH_2 [21,22], and (ii) NH_3 with acidic mineralizers, such as NH_4Cl [23]. Different behaviors are then observed, depending on the mineralizer nature. Basic mineralizers lead to a retrograde solubility [22], but the corrosion seems limited and Ni-based super-alloys are sufficient for building reaction vessels. Acidic mineralizers involve a normal solubility but the corrosion phenomena imply the use of Pt inner liner.

Due to the lack of natural single crystals, in the majority of cases, HVPE seeds were used. Different nutrients were tested, such as gallium metal, GaN, and a mixed Ga/GaN precursor.

The main problems from an economical point of view were: (i) the solubility of the nutrient and (ii) the growth rate of the GaN single crystal. Fukuda and Ehrentraut [16] have investigated the role of the solution composition (concentration of acidic mineralizer NH_4Cl) and the temperature ($250 \leq T \leq 550^\circ\text{C}$) on the molar solubility of GaN as nutrient. An important solubility value requires high temperature.

Another route would be to select a precursor more soluble than GaN or Ga in order to get an appropriate value at low or mild temperature conditions for, in particular, reducing the corrosion phenomena. A more ionic precursor, such as Li_3GaN_2 , was investigated by Goglio et al. [24]. The objective of such a research activity was to improve solubility and chemical transport in mild pressure and temperature conditions through the following reactions: $\text{Li}_3\text{GaN}_2 \rightarrow 3\text{Li}^+ + \text{GaN}_2^{3-}$ and $\text{GaN}_2^{3-} \rightarrow \text{GaN} + \text{N}^{3-}$ [25].

6. Development of new solvothermal processes for preparing functional materials

From an economical point of view, the lowering of the production cost of functional materials is an important challenge.

Among the functional materials, the superhard materials, such as diamond and c-BN with industrial developments, either as bulk materials or thin layers, need a reduction of their elaboration cost.

Different solvothermal approaches have been investigated for preparing diamond in mild pressure and temperature conditions [26–29]. In most cases, these approaches involved the diamond deposition on seeds. Recently, solvothermal diamond nucleation, growth, and sintering were proposed by Yamasaki and co-workers [30,31].

In parallel, c-BN synthesis was investigated through solvothermal processes [32] in order to reduce the experimental conditions, to induce the elaboration of single crystals and to verify the thermodynamical calculation of Solozhenko [33] or the experimental researches of Fukunaga et al. [34].

More recently metathesis reactions in solvothermal conditions were investigated by the research group from Shandong University (Jinan-RP China) [35–38].



Three main effects were studied to understand their influence on the obtained structural form of BN:

- (i) the role of temperature [36] (when temperature is increased $T > 480^\circ\text{C}$ the cubic phase is predominant),
- (ii) the nature of the halogen ($x = \text{Cl}, \text{Br}$) [37] (with $X = \text{Cl}$ cubic phase is preponderant),
- (iii) the impact of seeds for inducing the nucleation [38] (using BBr_3 as precursor (where c-BN is not the predominant product) but in presence of small seeds of GaP (with the zinc blende structure) the formation of cubic BN is only observed at 250°C and $P \approx 0.5 \text{ MPa}$).

If we compared the solvothermal conditions for c-BN formation with those of generally used ($P \geq 5$ GPa, $T \geq 1000$ °C) [39], solvothermal processes appear a promising route for preparing c-BN and other functional nitrides.

7. Conclusion

Solvothermal processes are powerful routes for developing nitrides. Four different domains could be developed in the near future.

- The synthesis of novel nitrides, in particular metastable nitrides, if the solvothermal reaction is kinetically controlled (through careful selection of chemical reactive precursors and mild temperature synthesis conditions).
- The preparation of nanocrystallites well defined in size and morphology. The induction of a functional morphology (as 1D) requires to control the crystal growth of the nuclei through different routes (capping agents, template, etc. [40]).
- The development of the solvothermal elaboration of single crystals – in particular, for nitrides characterized by specific physical properties (semi conductor, thermal conductivity, hardness, etc.) – appears an important challenge for improving industrial applications in different domains (opto-electronics, high frequency–high power electronics, micro-tooling, etc.).
- Solvothermal processes – due to the improvement of the chemical reactivity at the interface between the solvent and the precursors – can induce the development of novel elaboration processes of functional materials in economical conditions.

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