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Review

New Trends in Solvothermal Crystal Growth at the Macro- and Nanoscale

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Solvothermal processes, as compared to hydrothermal processes, enlarge the scope of the employed solvents from aqueous to non-aqueous media, the objective being to extend the possibilities for the preparation and/or the crystal growth of non-oxide materials. During the last fifteen years solvothermal crystal growth of materials has been investigated at two different levels: (i) the macroscopic scale, with the preparation of large single crystals of functional materials for specific applications, (ii) the nanoscale, involving the elaboration of single-crystalline nanocrystallites well defined in size and morphology, and particularly adapted to nanodevices. In the first domain, two main factors have been studied: (i) the influence of the thermodynamical parameters governing the solvothermal processes, and (ii) the purity of the components (nutrient, solvent, *etc.*), the main objective being to reduce drastically the density of defects inside the single crystals. In the second domain, strong efforts have been made: (i) to control the nano-size, but mainly, (ii) to induce specific morphologies, in particular 1D, appropriate to the relative nanotechnologies.

Key words: Solvothermal Crystal Growth, Large Single Crystals, Density of Defects, Nanoscale Crystal Growth, 1D Nanomorphology

Introduction

 α -Quartz – characterized by piezoelectric and optical properties leading to industrial applications – was historically used as a model material to develop the hydrothermal crystal growth process, strategic applications being supported by such a material [1–8]. Due to the structural transformation $\alpha \rightarrow \beta$ at a temperature of *ca.* 573 °C, the conventional crystal growth processes conducted at higher temperatures such as melt nutrient, gas-flux transportation, *etc.*, were impossible or difficult to apply to this α -quartz low-temperature form.

During the last thirty years, different compositions with a quartz-like structure such as AlPO₄, GaPO₄, GaAsO₄ [9–16] have been investigated. More recently two materials with a large spectrum of physical properties, GaN and ZnO, were developed as single crystals and wafers required for different applications [17, 18]. Considering the large variety of solvents already used or to be developed (in sub- or supercritical conditions) for the growth of single crystals in this context, the generic term "solvothermal" has been introduced.



Fig. 1. Schematic view of a solvothermal crystal growth equipment.

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The Solvothermal Crystal Growth of Large Single Crystals

Principle of the crystal growth process

The solvothermal crystal growth process of large single crystals involves the chemical transport – in a solvent – of chemical species issued from the partial dissolution of a chemical precursor (the nutrient) and their deposition onto seeds (with a specific structure).

The solubility of the nutrient depends on different factors: (i) the nature of the nutrient (composition, structure, *etc.*), and (ii) the thermodynamical parameters such as pressure (*P*) and temperature (*T*). For the deposition of the solvated chemical species, requiring a supersaturation in the vicinity of the seeds, the temperature gradient (ΔT) between the nutrient and the seeds plays an important role. ΔT can be positive ($T_{\text{dissolution}} > T_{\text{deposition}}$) or negative ($T_{\text{dissolution}} < T_{\text{deposition}}$) according to the thermal dependence of the nutrient solubility in the solvent (normal or retrograde solubility).

A schematic view of the high pressure vessel used for solvothermal crystal growth of large single crystals is given in Fig. 1 [7].

Main factors governing the solvothermal crystal growth process

These factors can be roughly classified into three types:

- *thermodynamical factors* such as: the pressure (*P*), the dissolution temperature ($T_{\text{diss.}}$), the crystal growth (T_{growth}) temperature, the temperature gradient (ΔT) and the hydrodynamics characterizing the system,
- chemical factors: the nature of the solvent and its physico-chemical properties [19], the nature of the nutrient (composition, structure), the nature of the seeds (orientation), and
- kinetical factors: the kinetics of nutrient dissolution, the diffusion of solvated chemical species into the solution, the crystal growth rate (some of these factors being interdependent).

Impact of the different factors governing the solvothermal crystal growth on the quality of the single crystals

The quality of a single crystal is generally assessed by its density of defects, two types of defects being taken into account: structural defects and chemical defects [20].

Structural defects concern all the imperfections observed between the as grown structure and the ideal structure. Such defects can be divided into macroscopic and microscopic according to their extension and the technique developed for their observation. Crevices, flaws and cracks observable without equipment can be considered as macroscopic structural defects. On the contrary, dislocations can be considered as microscopic defects (detected by X-ray topography).

Chemical defects involve the chemical substitution and/or insertion of foreign ions into the structure of the single crystal.

As an example, for an α -quartz single crystal, these chemical impurities can be classified into four types:

- macroscopically extended foreign chemical phases such as a solid or a liquid inclusion,
- microscopic chemical defects such as large ions having a small charge (Na⁺, Li⁺, K⁺, etc.) occupying the rather large interstitial channels parallel to the crystallographic c axis [21],
- hydrogen bound to oxygen in the structure (*i. e.* OH-Na⁺), and
- cations substituting Si^{4+} in the α -quartz structure (according to the charge of these cations, in particular for Al^{3+} , a charge compensation is required such as OH^- or Na^+ , for example).

Role of the crystal growth parameters leading to these defects

The growth rate

From an economical point of view, the highest growth rate is the most beneficial [22]. In the case of α -quartz, Martin and Armington reported the impact of the growth rate on the aluminum content as a chemical impurity [23]. The improvement of the growth rate leads to an increase of the aluminum concentration inside the α -quartz single crystal and also an increase in structural defects.

The growth rate function is modified by different physical, chemical and technical parameters [6] such as the pressure (*P*), the temperature gradient (ΔT), the concentration of the mineralizer in the solvent, the growth temperature (T_{growth}), the hydrodynamics of the system (such as the percentage of baffle open [24]),

the surface area of the nutrient and the seeds [25], as well as the orientation of the seeds. Among these parameters, ΔT seems predominant. Indeed Barns *et al.* demonstrated that the growth rate *R* was roughly a linear function of ΔT [26].

The chemical purity of the single crystal

The chemical impurities of the as grown single crystal can originate from three main factors: the nutrient, the chemical solvent and the interactions between the solvent and the high-pressure reaction vessel.

The nutrient

For α -quartz, using conventional solvents such as aqueous solutions of NaOH and Na₂CO₃ (≈ 1 M), different nutrients have been investigated, in particular α cristobalite, a polymorph of silica characterized by a higher solubility than α -quartz [27]. Such a structural form can be obtained in a high purity state with a low Al content [28]. The use of high-purity glass has also been described, but a recrystallization of the glass as α -quartz crystallites is usually required to control the dissolution process [29].

The solvent

Different solvents have been investigated in order to control the concentration of the chemical impurities, and in particular to reduce the chemical interactions with the walls of the high-pressure vessel [7].

New trends to improve the quality of large single crystals

The main challenges are the optimization of the growth rate *versus* the economical requirements, the quality of the as grown single crystals (including in particular the reduction of structural defects – in particular dislocations – and the reduction of the concentration of chemical impurities) and the management of all technical parameters governing the solvothermal process.

Optimization of the growth rate

The growth rate is dependent on many factors, and some of them can be optimized such as the pressure and the growth temperature. Some preliminary experiments have demonstrated the role of pressure for the growth rate and the quality of the resulting α -quartz single crystals. The α_{3500} IR coefficient (to evaluate the concentration of OH groups in the crystal [30])



Fig. 2. Influence of the pressure on the growth rate of α -SiO₂ (a) and on the effects in the IR characterization (b). Solvothermal growth conditions: Solvent 1 M NaOH, $T_{\text{growth}} = 350 \text{ °C}$, $\Delta T = 10 \text{ °C}$, duration: 10 days [36].

is reduced upon an increase of pressure. This phenomenon is correlated with the decrease of aluminum insertion through the following chemical substitutions (cationic and anionic) characterizing the charge equilibrium: $Al^{3+} \rightarrow Si^{4+}$ and $OH^- \rightarrow O^{2-}$ (Fig. 2).

The same reduction of the α_{3500} IR coefficient is observed when the growth temperature is increased (Fig. 3).

Consequently, the management of these two parameters (crystal growth at higher pressure and temperature) can lead to new solvothermal crystal growth processes with an optimization of the growth rate and of the density of chemical defects.



Fig. 3. Evolution of the IR coefficient α_{3500} versus T_{growth} for α -quartz [36].

The role of lithium on the growth rate must be reinvestigated. A preliminary NMR study on the crystal growth of α -quartz has shown that Li⁺ was mainly localized at the interface of the growing film [31]. Some recent work on the solvothermal crystal growth of ZnO confirmed the role of Li⁺ as a crystal growth moderator [32, 33].

Improvement of the quality of as grown single crystals The reduction of dislocations

Using mild ΔT values, the density of dislocations is mainly correlated to those of the seeds. The crossrecrystallization can be a route to reduce the density of dislocations in the seeds. Different seed orientations have also been selected in the case of α -quartz [34].

The reduction of the chemical impurities

The pressure value and the growth temperature play an important role in the insertion of chemical impurities (as Al^{3+} for α -quartz) into the single crystal [35, 36].

Two others routes can lead to improvements:

- the purification of the nutrient (throught a multirecrystallization) [37] and
- the reduction of the mineralizer concentration, even the use of pure solvents such as water [38].

The control of the technical parameters

Control of the growth rate during the experiment

Due to the increase in size of the single crystal during the solvothermal growth process, the deposition rate must be optimized in order to secure the homogeneity of the crystal [25].

The optimization of the ΔT value for the crystallization time has recently been investigated for α -quartz in order to adjust the growth rate [39]. Using additives for a control of the adsorbed film of solvent at the growing interface could be a way to manage the growth rate [40].

Hydrodynamics of the system

The baffle plays an important role to control the hydrodynamics. Bulk flow of solution in a hydrothermal autoclave has been investigated using different numerical analyses of turbulent natural convection [41, 42].

Development of solvothermal crystal growth for the elaboration of single crystals

During the last ten years, solvothermal crystal growth has been developed to prepare single crystals, in particular of two materials, GaN [43–46] and ZnO [47–53], owing to their importance in different industrial domains such as electronics, optoelectronics, spintronics, *etc.* [54, 55]. In both cases, the solvothermal process has been selected because of the mild temperature conditions required for the crystal growth compared to conventional processes. The developments for α -quartz also facilitate the scaling-up of the processes. In the case of ZnO, different crystal growth methods can lead to large single crystals, but the solvothermal process is preferred due in particular to the lowest concentration of defects achieved [55].

For the applications involving piezoelectric properties, Langasite-type crystals (LGS, LGN, LGT, SGG) have attracted much attention for their applications in surface acoustic wave (SAW), bulk acoustic wave or sensors fields [56, 57]. Using conventional crystal growth processes, the congruent points characterizing such compositions are not located at their stoichiometric composition. Among the langasite-type compounds, few have been found with an ordered langasite structure [58] [Sr₃MGa₃Si₂O₁₄ with M = Nb (SNGS) or M = Ta (STGS), $\text{Ca}_3M\text{Ga}_3\text{Si}_2\text{O}_{14}$ with M = Nb(CNGS) or Ta (CTGS)]. Until now, few reports concerning the growth and characterization of ordered single crystals are available [59]. Using the Czochralski process, single crystals of Ba₃TaGa₃Si₂O₁₄ [60] and Ca₃TaGa₃Si₂O₁₄ [61] have been prepared. With the main growth defects attributed to the high viscosity of

the melt, the solvothermal process appears to be an interesting growth technique for the future in order to reduce the density of such defects.

Solvothermal processes have also been developed to prepare single crystals of materials with specific physical properties for industrial applications such as KBe₂BO₃F₂, ZSM-5 zeolithe, γ -LiBO₂, KTP, calcite, on hydroxyapatite [62–67].

The Solvothermal Crystal Growth at the Nanoscale

During the last decade, strong interest has focused on low-dimensional materials, in particular nanocrystallites, due to their unique physical properties and related potential applications in different domains [68-72]. Different morphologies such as wires, rods, tubes, *etc.* are required for nanoscale devices [73,74]. Solvothermal processes have been investigated to reach such specific shapes, in particular the development of 1D morphologies [75].

Among the different preparative routes which allow a control of the crystal growth of nanocrystallites through solvothermal processes, four have mainly been developed:

- the "structure inherent solid state reaction" with topotactic solvothermal reactions between the precursors and the final product,
- the induction of a specific shape using templates,
- the modification of the surface energy of specific crystallographic planes of the nuclei, and
- the self-assembly of nanoparticles along a crystallographic direction.

The selection of the nature (composition and structure) of the precursors can play an important role in determining the structure and the morphology of the resulting nanocrystallites if one of the reactants remains in the solid state and can act as a "pseudo-template" [76].

Solvents have been investigated with different objectives: (i) the stabilization of intermediate chemical species can induce an anisotropic shape with either the formation of an intermediate "solvent coordination molecular template" (SCMT) such as ZnS·0.5 en (en = ethylenediamine) during the synthesis of ZnS [77], or the stabilization of an intermediate phase such as $H_2K_2Ti_6O_{14}$ during the preparation of $K_2Ti_6O_{13}$ nanowires [78]; (ii) the control of the kinetics of the chemical reaction can modify the crystal growth of the nanoparticules [79]; (iii) the adsorption of functional

groups characteristic for the solvent on some specific surfaces of the nuclei can induce specific morphologies [80, 81]; (iv) the specific physico-chemical properties of the solvent, such as ionic liquids, help to control the morphology [82].

Specific precursors can be developed as templates for inducing the 1D morphology. This is the case in particular in the conversion of ZnO nanorods into tubular ZnO/ZnS core/shell nanocomposites through a hydrothermal sulfidation treatment using thioacetamide (TAA) as sulfur source [83], or also in the preparation of tubular SiO₂ nanosystems through an hydrothermal reaction of BaSiF₆ nanorods in alkaline solutions [84].

Capping surfactants have also been investigated. Oleic acid in particular was chosen to prepare TiO_2 nanorods because its carboxylic acid functional groups are able to tightly bind onto the TiO_2 surface of the nuclei [85, 86].

Biomolecules have attracted much interest during the last years due to their ability to interact with chemical species with the typical size-matching for the nanoscale dimensions through their specific chemical groups (-COOH and -NH₂ for amino acids) [87]. Different functions have been attributed to such biomolecules: (i) as a directional template to prepare, for example, single-crystalline tellurium nanowires using alginic acid [88], or single-crystalline selenium with β -carotene [89], or (ii) as a self-assembly agent [90].

Due to the relevance of nanodevices with singlecrystalline 1D nanocrystallites, solvothermal growth processes at the nanoscale will be developed in the near future to induce specific shapes well adapted to different nanodevices.

Conclusion

Solvothermal processes are important crystal growth techniques with many advantages compared to the conventional methods due in particular to the use of mild temperature and pressure conditions.

At the macroscale, the solvothermal growth of single crystals can lead to a reduction of the chemical and physical defects compared to the conventional processes (chemical vapor transport (CVT), flux method, melt growth method, *etc.*). The industrial demand of: (i) a low density of defects in single crystals, and (ii) a rapid scale-up, will lead to a development of this growth technique in the near future in particular for different functional materials characterized by specific physical properties.

At the nanoscale, the preparation of singlecrystalline nanocrystallites, in particular with 1D morphologies, appears to be an important challenge to enhance the development of nanodevices [91,92]. In such

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a domain the investigations on the role of the different components (physical-chemical properties of the solvents, composition and structure of the reactants and additives and their interactions with the nuclei) must be continued.

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