

Review

## Solvothermal Processes: Definition, Key Factors Governing the Involved Chemical Reactions and New Trends

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Solvothermal processes are defined, and the different domains of applications are described. The main physico-chemical factors playing a key role in such processes are then analyzed. The trends characterizing the current development of solvothermal processes are outlined.

*Key words:* Hydrothermal Processes, Aqueous Solvents, Solvothermal Processes, Non-aqueous Solvents, Key Factors

### Introduction

A solvothermal process can be defined as a process in a closed reaction vessel inducing a decomposition or a chemical reaction(s) between precursor(s) in the presence of a solvent at a temperature higher than the boiling temperature of this solvent. The pressure can be autogeneous (in such a case the pressure value depends on the filling of the reaction vessel) or imposed (the pressure value being higher than 1 bar ( $10^5$  Pa) at the starting point of the experiment through the compression of the reaction medium). Depending on the experimental conditions (pressure and temperature), the solvothermal system can be heterogeneous or homogeneous and in subcritical or supercritical conditions.

The word “solvothermal” can be used whatever the chemical composition of the solvent is (aqueous or non-aqueous) [1]. Originally such processes were developed with water, due to its importance on the surface of the earth. For aqueous solutions the word “hydrothermal” is commonly used [2, 3].

Hydrothermal processes were first developed in geosciences with the synthesis of minerals [4], in materials science with the crystal growth of functional materials [5, 6], and in hydrometallurgy for developing new methods for leaching ores [7].

During the last ten years solvothermal processes have been extensively used in different domains:

– materials chemistry with the synthesis of novel ma-

terials [8], in particular metastable phases through the improvement of the kinetics [9],

- molecular chemistry with the synthesis of new polymers [10],
- hybrid chemistry with the stabilization of novel frameworks [11], through the preparation of materials involving inorganic/organic components [12] or inorganic/biological components [13],
- materials science involving different important areas:
  - the elaboration of nanocrystallites [14] or more recently nano-systems [15],
  - the crystal growth of functional materials characterized by specific physical properties supporting industrial applications [16],
  - the deposition of thin films [17], and
  - the preparation of ceramics using low temperature conditions [18],
- biotechnology with the development of bioinspired nano-functional systems [19].

### Main Physico-Chemical Factors Governing Solvothermal Reactions

Taking into account the definition of a solvothermal process, the factors playing a key role can be divided into different classes.

*Chemical factors*

- the chemical nature of the solvent and its physico-chemical properties,
- the chemical composition, structure and properties of the precursors,
- the nature of the additives, and
- the pH value of the reaction medium.

*Thermodynamical factors*

- the temperature and
- the pressure.

*The associated technologies employed*

- microwaves,
- electrochemistry,
- external magnetic field,
- ultrasound, and others.

*Factors controlling the mechanisms of the involved chemical reactions*

In addition, during the last years the mixing mode of the reactants and its impact on the reaction mechanisms characterizing solvothermal processes have been investigated, as for example:

- solvothermal pressure relief where the amount of gas produced in the high-pressure vessel is controlled [20],
- solvothermal scission-template-transportation with the formation of an intermediate compound acting as a template [21],
- solvothermal extraction [22],
- phase-transfer catalysis [23], and
- high-temperature mixing methods [24].

**The Role of the Solvent in Solvothermal Processes**

For reactions in a liquid phase, the solvent can play different roles through its physico-chemical properties: (i) it can control the concentration of the chemical species in the solution affecting the kinetics of the reaction, and (ii) it is able to modify the coordination of solvated species and induce specific structures.

The stabilization, through solvothermal processes, of the different MnS structural forms has been investigated during the last ten years. Manganese sulfide can exist with three different structures: two metastable ( $\gamma$  and  $\beta$ ) and one stable ( $\alpha$ ).

With the same reactants [ $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_2)_2\text{CS}$ ], different structures have been stabilized according to the chemical nature of the solvent. Metastable forms ( $\gamma$  and  $\beta$ ) have been observed with tetrahydrofuran and benzene, but the stable  $\alpha$  rocksalt form is prepared using water or ethylenediamine. The stabilization of a specific structural form is induced by the kinetics of the solvothermal reaction. Solvents which favor the formation of intermediate Mn complexes (such as water or ethylenediamine) can slow down the kinetics and consequently lead to the formation of the thermodynamically stable  $\alpha$  form. On the contrary, with solvents such as tetrahydrofuran or benzene, unable to induce the complexation of  $\text{Mn}^{2+}$ , the kinetics is fast, and metastable structural forms can thus be obtained [25].

The physico-chemical properties of the solvent can be modified using mixed solvents. Such modifications can play an important role in the nucleation and the crystal growth steps. Indium tin oxide (ITO) is an important material with many electronic and optical applications due to high electrical conductivity and high transparency [26, 27].

A solvothermal process using hydrated indium nitrate [ $\text{In}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ] and tin (IV) chloride [ $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ] as reactants and  $\text{NH}_4\text{OH}$  as the mineralizer has been studied. The resulting precipitate, after drying, was treated under solvothermal conditions (250 °C, autogeneous pressure) using different solvents: ethyleneglycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), polyethylene glycol [ $\text{H}(\text{OC}_2\text{H}_4)_n\text{OH}$ ] and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ). TEM analysis has shown that the solvent viscosity determines the size and the physico-chemical properties of the resulting ITO crystallites. The increase of the viscosity [from  $\text{C}_2\text{H}_5\text{OH}$  to  $\text{H}(\text{OC}_2\text{H}_4)_n\text{OH}$ ] enhances the crystal growth rate compared to the nucleation rate and in parallel induces the formation of oxygen vacancies leading to more free electrons and higher conductivity [28].

With the development of nanocrystallites through solvothermal processes, different studies have underlined the role of the physico-chemical properties of the solvent on the size and the morphology of the resulting particles. The influence of ethylenediamine (en) and water (or mixed  $\text{H}_2\text{O}/\text{en}$  solvents) on the

morphology of CdS nanoparticles was studied using  $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_2)_2\text{CS}$  (or  $\text{Na}_2\text{S}$ ) as sulfur sources. Without ethylenediamine, a spherical morphology was detected, but with the addition of (en) more accelerated growth along the  $\langle 001 \rangle$  direction was observed [29]. The formation of such nanorods was explained by the complexation in  $[\text{Cd}(\text{en})_3]^{2+}$ . The existence of an intermediate compound ( $\text{CdS} \cdot 0.5\text{en}$ ) with a 3D network could initiate, as a template, the elongated morphology of CdS nanocrystallites [30].

Solvent effects are also important in solvothermal processes involving organic chemicals. Biodegradable polymers have recently gained more attention as a potential substitute for conventional synthetic petroleum-based polymers [31]. Poly(L-lactide) (PLAs) was obtained from the ring-opening polymerization of L-lactide through a solvothermal process using  $\text{SnCl}_2$  as the catalyst for the polymerization reaction. The nature of the solvent is one of the important factors because it can promote the solubility and reactivity of compounds and complexes at elevated temperatures under high pressure [10].

These examples have demonstrated that the selection of the chemical nature of the solvent appears to be an important factor, allowing to control the resulting structural form in materials chemistry or to direct the morphology of the nanocrystallites in materials science.

### The Role of the Chemical Nature of the Reactants in Solvothermal Processes

#### *Impact of the solubility of the reactants*

In materials chemistry, for the same solvent, the reaction can be governed by the concentration of chemical species in the reaction medium, this concentration being directly correlated to the solubility of the reactants.

In the solvothermal synthesis of CdS using ethylenediamine as the solvent, the same cadmium precursor ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) but different sulfur sources [ $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , thiourea, sulfur] can be selected as an illustration [32]. The nature of the sulfur source plays an important role either on the CdS crystal structure or the morphology of the resulting crystallites. Such results can be explained by the reaction process in two steps:

- (1)  $\text{Cd}^{2+} + 3\text{en} \rightarrow [\text{Cd}(\text{en})_3]^{2+}$
- (2)  $[\text{Cd}(\text{en})_3]^{2+} + \text{S}^{2-} \rightarrow \text{CdS} + 3\text{en}$ .

The structure and consequently the morphology of the resulting CdS crystallites is induced by the release of  $\text{S}^{2-}$  into the reaction medium. With  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , due to its solubility leading to a high  $\text{S}^{2-}$  concentration, the kinetic factor induces the formation of the metastable zinc blende structure. On the contrary, with thiourea and sulfur, the slow release of  $\text{S}^{2-}$  favors the thermodynamically stable wurtzite form.

#### *Solvothermal topotactic reactions induced by quasi-insoluble reactants*

In the majority of cases, solvothermal processes involve the dissolution of the reactants. Consequently, all structural correlations between reactants and products are lost, and only chemical species in the solution can play a role.

If one of the reactants remains in the solid state under solvothermal conditions (in particular for low-temperature syntheses) it becomes possible to initiate the structure of the final product through the insoluble reactant. Such a solvothermal route was called “structure-inheriting solid-state reaction” by Whittingham [33]. The synthesis of  $\text{CoMoO}_4$  through a solvothermal process (using water as the solvent) was investigated as a function of the reaction time using  $\text{MoO}_3$  and  $\text{CoO}$  as precursors at 453 K.  $\text{MoO}_3$  is completely dissolved within the first step ( $\sim 5$  min) of the hydrothermal treatment leading to the formation of  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$ . Upon increasing reaction time, the high-pressure form of  $\text{CoMoO}_4$  (hp- $\text{CoMoO}_4$ ) appears, accompanied by a gradual disappearance of  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$ . hp- $\text{CoMoO}_4$  is the most dense form of the three structural forms ( $\alpha$ ,  $\beta$ , hp- $\text{CoMoO}_4$ ). Consequently  $\text{CoMoO}_4 \cdot 3/4\text{H}_2\text{O}$  initiates the hp form through a pseudo-topotactic reaction during the hydrothermal process.

#### *Stabilization of intermediate species as templates through solvent/reactants interactions*

The chemical interactions between reactants and solvent can induce the formation of intermediate species which are able to influence the morphology of the resulting crystallites.

For example, during the solvothermal synthesis of metal selenide crystallites, using metal chlorides (or nitrates) and selenium powder as reactants and hydrazine hydrate as the solvent, the formation of an intermediate species has been suggested to explain the observed 1D morphology of the resulting crystallites [34]. The

NH<sub>2</sub>-NH<sub>2</sub> group may act as a bridging bidentate ligand between two different cationic clusters and lead to intermediate species able to initiate a 1D morphology.

*Formation of intermediate compounds which are able to modify the kinetics of the reaction*

In some cases, the intermediate chemical species stabilized during the solvothermal reaction are able to modify, according to their stability, the kinetics. Consequently, the phase evolution to the final crystallites can modify the nucleation and the crystal growth steps and therefore their size and morphology.

The preparation of yttrium aluminum garnets (YAG) using a solvothermal process with ethylenediamine as the solvent and yttrium and aluminum nitrates as reactants can be used as an illustration [35].

Two different precipitants have been used to produce hydroxides as precursors: urea and ammonium hydrogen carbonate. With urea, the formation of YAG implies a transitory step with the intermediates YAlO<sub>3</sub> and Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>, but with ammonium hydrogencarbonate, hydroxides are directly converted to the pure YAG phase. In this last case, a better dispersity and smaller crystallites are observed.

**The Role of Different Additives used in Solvothermal Processes**

Additives have mainly been used for governing the morphology of the obtained crystallites through solvothermal processes. Several types of additives with different effects have been developed in the last ten years mainly to induce specific morphologies of nanoparticles:

- capping agents (polymers [36], alkylamine [37], CTAB [38]),
- biomolecules as structure-directing agents due to their ability to interact with chemical groups (in particular COOH<sup>-</sup>, NH<sub>2</sub>) through a typical size matching at the nanoscale [39],
- mineralizer-assisted processes in particular for inducing a specific structural form or for improving the crystal growth [40, 41], and
- oxido-reduction syntheses (reductants [42] or oxidants [43]).

In some cases, biomolecules can be used as reactants, as for the synthesis of CdS nanowires from CdCl<sub>2</sub> · 2,5H<sub>2</sub>O and L-cysteine in presence of

ethanolamine and water as solvents [44]. L-Cysteine acts both as the sulfur source and the coordinating agent due to the presence of NH<sub>2</sub> and HS groups.

**The Role of the pH Value in Different Solvothermal Processes**

For processes in solution, in particular solvothermal processes, the pH value can play different roles [45–47].

For example, it can

- help in the preparation of specific compositions in materials synthesis,
- induce the stabilization of specific structural forms,
- control the size and the morphology of the crystallites, or
- facilitate the elaboration of nanocomposites.

In particular the influence of the pH value on the coordination geometry of the transition metal and the coordinating mode of the ligands has been investigated for the synthesis of hybrid materials between transition metals and polymers.

**Impact of the Thermodynamical Parameters: Temperature and Pressure**

*The role of temperature*

In solvothermal reactions, temperature can modify different factors: the kinetics of the chemical reaction, the solubility of the precursors, the stability of the reactants (through solvothermal decomposition), the chemical composition of the solvent (through its partial decomposition), the formal oxidation state of the transition metals *etc.*

As an illustration, the synthesis of some mixed Na/V and K/V fluorides or oxyfluorides was investigated by solvothermal methods using a water/ethylene glycol mixture as the solvent [48]. At a temperature close to 100 °C the formation of oxyfluoride phases containing V<sup>4+</sup> (NaV<sub>2</sub>O<sub>2</sub>F<sub>8</sub> and K<sub>2</sub>VOF<sub>4</sub>) is observed. By raising the temperature to 220 °C, the reduction of V<sup>4+</sup> to V<sup>3+</sup> induces the stabilization of the fluorides KVF<sub>4</sub> and K<sub>5</sub>V<sub>3</sub>F<sub>14</sub>.

When the temperature is increased, solvent decomposition can take place. This is the case in the solvothermal synthesis of Ta<sub>3</sub>N<sub>5</sub>. Using TaCl<sub>5</sub> and LiNH<sub>2</sub> as the reactants in the presence of benzene as solvent the formation of Ta<sub>3</sub>N<sub>5</sub> nanocrystallites was

observed in the temperature domain 500–550 °C. With the same reactants, but replacing benzene by mesitylene as solvent, a higher crystallization temperature is required. This temperature increase leads to a large amount of carbon incorporated in the nitride structure due to solvent decomposition [49].

In molecular chemistry, paramagnetic clusters are prepared through conventional processes using the mixing of metal ions and ligands in a common solvent at a temperature limited by the boiling point of this solvent at atmospheric pressure. New preparative routes based on solvothermal methods have been developed at higher temperatures [50–52].

Recently the effect of the cooling rate was demonstrated in the solvothermal synthesis of ZnO nanorods [53].

#### *The role of pressure*

In solvothermal processes, pressure can play different roles: (i) the stabilization of more dense structures, if the pressure range is large enough, (ii) the enlargement of the thermal stability domain of the reactants, and (iii) the enhancement of the chemical reactivity and of the kinetics of the involved reactions.

The solvothermal synthesis of  $\text{Sb}_2\text{S}_3$  from  $\text{SbCl}_3$  with thiourea as the sulfur source and methanol as the solvent can be used as an illustration of a pressure-controlled formation of nanorods [54].

The solvothermal preparation of CuO and  $\text{Cu}_2\text{O}$  nanocrystallites using Cu(II) acetate,  $\text{Cu}(\text{CH}_3\text{COO})_2$ , as the precursor and water as the solvent was investigated depending on the imposed pressure value. The pressure increase seems both to hinder the effectiveness of the reduction phenomenon induced by  $\text{CH}_3\text{COOH}$  (with the partial formation of CuO) and to affect the morphology of the crystallites [55].

#### **Associated Technologies**

Associated technologies (electrochemistry, microwaves, sonochemistry, flow reaction, mechanical mixing, high-temperature mixing *etc.*) are used to modify the chemical reactivity of the reactants and consequently the kinetics of the solvothermal reactions [56–60]. For a liquid phase, the energy supplied by temperature must be compared to that arising from the pressure parameter [61].

Different studies were carried out on the effects of microwaves in solvothermal reactions in different scientific domains (materials chemistry, synthesis of nanocrystallites, hybrid materials). Microwave irradi-

ation is a fast internal heating able to induce a fast nucleation.

Some correlations have recently been delineated between the microwave power and the morphology of ZnSe crystallites (a material for optoelectronic devices) [62]. Using the same experimental conditions (nature of the reactants, nature of the solvent, temperature and pressure conditions), the anisotropy of the ZnSe crystallites increases with the microwave power.

To prepare hybrid materials, the comparison of conventional heating and microwave heating has shown that the crystalline quality and the yield of the product are obviously better with a shortened reaction time [63].

Combined sonochemical-solvothermal processes have also been developed in particular to prepare nanocrystallites and metal organic frameworks (MOFs) [64, 65].

#### **Associated Methods to Prepare the Reaction Medium**

Different methods for the preparation of the reaction medium have been investigated during the last years, in particular in materials chemistry (synthesis of new materials) and materials science (to obtain nanoparticles with controlled size and morphology), for example

- solvothermal pressure-relief where the gas produced in the high-pressure vessel is controlled [66],
- solvothermal scission-template-transportation with the formation of an intermediate compound acting as the template [67],
- extraction solvothermal methods [68],
- phase-transfer catalysis [69],
- sol-solvothermal processes where the mixture of precursors is prepared as a sol [70],
- hydrothermal processes assisted by microemulsion techniques [71].

An interesting illustration in the synthesis of materials is the result of an investigation of the impact of the way sodium azide ( $\text{NaN}_3$ ) was introduced during the hydrothermal preparation of cubic BN using boric acid ( $\text{H}_3\text{BO}_3$ ), sodium azide ( $\text{NaN}_3$ ), hydrazine hydrate ( $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{O}$ ), and trimethylamine ( $\text{N}(\text{CH}_3)_3$ ). Defining the ratio  $R_N = (\text{NaN}_3)_I / (\text{NaN}_3)_{II}$ , where  $(\text{NaN}_3)_I$  denotes the amount of sodium azide introduced into the autoclave at the beginning of the reaction process and  $(\text{NaN}_3)_{II}$  the quantity of sodium azide

introduced into the autoclave at 300 °C and 10 MPa, the content and crystallinity of *c*-BN can be improved by increasing the  $R_N$  value [72].

### Recent Trends in Solvothermal Processes

According to recently published papers, different research domains have been strongly involved in the development of solvothermal processes.

#### *Synthesis of novel materials*

During the last twenty years mainly oxides, fluorides or nitrides have been prepared through solvothermal routes [73]. New preparation methods have recently been developed, in particular for the synthesis of sulfides [74], the elaboration of oxynitrides [75], and to set up fluorination processes [76]. In addition, a strong interest has been focused on the solvothermal synthesis of carbon, in particular carbon sheets, carbon nanotubes and graphene [77–79].

#### *Development of new solvents*

Ionic liquids appear to be functional solvents for the preparation of nanocrystallites due to their specific physico-chemical properties and their use as potential templating and structure-directing agents [80,81]. In addition, different bi-fonctionnal solvents have been developed as complexing and reducing agents (in particular to stabilize metallic nano particles) [82].

#### *Elaboration of nano crystallites*

Nanocrystallites well defined in size but with specific morphologies, in particular nanophosphors [83,84], nanotubes [85,86] and nanocomposites [87,88], have attracted great interest in recent years.

#### *Solvothermal processes in biochemistry*

The impact of hydrothermal reactions in biochemistry is an important challenge either for a better understanding of the origin of life [89–91] or for the development of new original routes to biomolecules [92].

#### *Synthesis of hybrid materials*

Hybrid materials such as inorganic/organic, with an emphasis on the stabilization of novel structures [93], or inorganic/biological, with specific properties, represent an important challenge for the future [94].

#### *Development of hydro/solvothermal crystal growth processes*

The preparation of single crystals for functional materials is always an important domain for various industrial applications. In particular GaN and ZnO have received increasing interest from both fundamental and technological points of view [95–98].

#### *Preparation of thin films through solvothermal processes*

During the last years, solvothermal routes have been developed to thin films using different types of substrates to produce particles of good homogeneity in size and morphology [99,100].

### Conclusion

Hydrothermal crystal growth (in particular of  $\alpha$ -quartz) and hydrothermal leaching of ores in metallurgical processes were, at the beginning of the 20<sup>th</sup> century, the first developments of aqueous solutions under mild-temperature and high-pressure conditions.

During the last twenty years, two main aspects have characterized these processes: (i) the opening to non-aqueous solvents in particular for the preparation of non-oxide systems leading to the generic term solvothermal and (ii) the development of such processes in different domains in particular due to the mild-temperature conditions (for example the synthesis of hybrid-materials, the preparation of nano-system, etc.).

One of the important challenges in the future will be the stabilization of hybrid systems including biological components such as proteins and amino acids. In such a way, solvothermal processes could play an important role in the preparation of bionanodevices, the mild conditions being apt to preserve the functions of biological components within artificial environments [101].

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[1] G. Demazeau, O. Martel, M. Devalette, E. Verdon, EP 238367, **1987**

[2] H. P. Eugster, *Am. Mineral.* **1986**, *71*, 655–673.

[3] S. Tsuboi in *Proceedings of the First International Symposium on Hydrothermal Reactions* (Ed.: S. Somiya), Gakujutsu Bunken Fukyu-kai, TIT, Tokyo **1982**.

- [4] R. M. Barrer, E. A. D. White, *J. Chem. Soc. (London)* **1951**, 1267–1278 (part I); *ibid.* **1952**, 1561–1571 (part II); *ibid.* **1953**, 1466–1475 (part III).
- [5] K. F. E. Schafhäütl, *Gelehrte Anzeigen Bayer Akad.* **1845**, 20, 557, 561, 569, 593.
- [6] G. Spezia, *Atti. Acad. Sci (Torino)* **1898**, 33, 157; *ibid.* **1905**, 40, 254–255; *ibid.* **1906**, 41, 158.
- [7] F. Habashi, *Rev. High Pressure Sci. Technol.* **1998**, 7, 1401–14.
- [8] R. Roy, O. F. Tuttle, *Phys. and Chem. Earth* **1956**, 1, 138–180.
- [9] Y. J. Li, M. S. Whittingham, *Solid State Ionics* **1993**, 63, 391–395.
- [10] L. Fang, R. Qi, L. Liu, G. Juan, S. Huang, *Int. J. Polymer Sci.* **2009**, 2009, article ID 929732 (7 pages).
- [11] X. M. Chen, M. L. Tong, *Acc. Chem. Res.* **2007**, 40, 162–170.
- [12] C. N. R. Rao, A. K. Cheetham, A. Thirumuragan, *J. Phys.: Condensed Matter* **2008**, 20, 083202 (21 pages).
- [13] E. Katz, I. Willner, *Angew. Chem.* **2004**, 116, 6166–6235; *Angew. Chem. Int. Ed.* **2004**, 43, 6042–6108.
- [14] K. Byrappa, T. Adschiri, *Progr. Crystal Growth Character. Mater.* **2007**, 53, 117–166.
- [15] R. Psaro, M. Guidotti, M. Sgobba in *Inorganic and Bio-inorganic Chemistry* (Ed.: I. Bertini), in *Encyclopedia of Life Support Systems* **2006**, chapter 14.
- [16] K. Byrappa, M. Yoshimura, *Handbook of Hydrothermal Technology: A Technology for Crystal Growth and Materials Processing* William Andrew Publishing, Noyes, **2001**.
- [17] M. Takeshi, *Electromagn. Symp. Proc.* **2004**, 16, 1–6.
- [18] N. Yamasaki, T. Kai, M. Nishioka, K. Yanagisawa, K. Ioku, *J. Mater. Sci. Lett.* **1990**, 9, 1150–1151.
- [19] M. Darder, P. Aranda, E. Ruiz-Hitzky, *Adv. Mater.* **2007**, 19, 1309–1319.
- [20] C. H. Yu, Z. H. Han, J. Yang, H. Q. Zhao, R. Y. Yang, Y. Xie, Y. T. Qian, Y. H. Zhang, *Chem. Mater.* **1999**, 11, 192–194.
- [21] J. Lu, Y. Xie, G. Du, X. Jiang, L. Zhu, X. Wang, Y. Qian, *J. Mater. Chem.* **2002**, 12, 103–106.
- [22] S. Huaqiang, Z. Xiaodong, X. Fu, W. Debao, H. Zhengsdai, *Mater. Lett.* **2006**, 60, 1793–1795.
- [23] M. Wen, H. Qi, W. Zhao, J. Chen, L. Li, Q. Wu, *Colloids and Surfaces: Physico-Chem. Eng. Aspects* **2008**, 312, 73–78.
- [24] L. Bai, K. Zhu, L. Su, J. Qiu, H. Ji, *Mater. Lett.* **2009**, 64, 77–79.
- [25] J. Mu, Z. Gu, L. Wang, Z. Zhang, H. Sun, S. Z. Kang, *J. Nanopart. Res.* **2008**, 10, 197–201.
- [26] J. H. Hwang, D. D. Edward, D. R. Kammler, J. O. Mason, *Solid State Ionics* **2000**, 129, 135–144.
- [27] C. P. Udawatte, K. Yanagisawa, *J. Solid State Chem.* **2000**, 154, 444–450.
- [28] J. S. Lee, S. C. Choi, *J. Europ. Ceram. Soc.* **2005**, 25, 3307–3314.
- [29] F. H. Zhao, Q. Su, N. S. Xu, C. R. Ding, M. M. Wu, *J. Mater. Sci.* **2006**, 41, 1449–1454.
- [30] Z. X. Deng, L. Li, Y. Li, *Inorg. Chem.* **2003**, 42, 2331–2341.
- [31] S. Mecking, *Angew. Chem.* **2004**, 116, 1096–1104; *Angew. Chem. Int. Ed.* **2004**, 43, 1078–1085.
- [32] F. Li, W. Bi, T. Kong, C. Wang, Z. Li, X. Huang, *J. Alloys Compd.* **2009**, 479, 707–710.
- [33] K. Eda, Y. Uno, N. Nagai, N. Sotani, C. Chen, S. Whittingham, *J. Solid State Chem.* **2006**, 179, 1453–1458.
- [34] Y. Liu, J. Cao, C. Li, J. Zeng, K. Tang, Y. Qian, W. Zhang, *J. Am. Ceram. Soc.* **2006**, 89, 2926–2928.
- [35] Z. Wu, X. Zhang, W. He, Y. Du, N. Jia, P. Liu, F. Bu, *J. Alloys Compd.* **2009**, 472, 576–580.
- [36] J. H. Zhan, X. G. Yang, S. D. Li, D. W. Wang, Y. Xie, Y. T. Qian, *J. Crystal Growth* **2000**, 220, 231–234.
- [37] P. Li, L. Wang, L. Wang, Y. Li, *Chem. Eur. J.* **2008**, 14, 5951–5956.
- [38] D. Liang, S. Tang, J. Liu, J. Liu, X. Lv, L. Kang, *Mater. Lett.* **2008**, 62, 2426–2429.
- [39] F. Gao, Q. Lu, X. Meng, S. Komarneni, *J. Mater. Sci.* **2008**, 43, 2377–2386.
- [40] Y. Huang, J. Wu, Y. Wie, J. Lin, M. Huang, *J. Alloys Compd.* **2008**, 456, 364–367.
- [41] X. Zhu, J. Ma, J. Tao, J. Zhou, Z. Zhao, L. Xie, H. Tian, *J. Am. Ceram. Soc.* **2006**, 89, 2926–2928.
- [42] T. Dubois, G. Demazeau, *4<sup>th</sup> International Symposium on Hydrothermal Reactions*. (Eds.: M. Cuney, M. Cathelineau), Nancy, **1993**, pp. 39–41.
- [43] G. Demazeau, P. Maestro, T. Plante, M. Pouchard, P. Hagenmuller, *Ann. Chim. Sc. Matér.* **1978**, 3, 353–359.
- [44] X. L. Liu, Y. J. Zhu, *Mater. Lett.* **2009**, 63, 1085–1088.
- [45] M. Taliakos, E. Katsoulakou, A. Terzis, C. Raptopoulou, P. Cordopatis, E. Manessi-Zoupa, *Inorg. Chem. Commun.* **2005**, 8, 1085–1089.
- [46] C. Qian, G. Liu, T. Okamura, Y. Huang, W. Sun, N. Ueyama, *Polyhedron* **2008**, 27, 812–820.
- [47] Q. Yu, X. Zhang, H. Bian, H. Liang, B. Zhao, S. Yan, D. Liao, *Crystal Growth & Design* **2008**, 8, 1140–1146.
- [48] D. W. Aldous, Ph. Lightfoot, *Solid State Sci.* **2009**, 11, 315–319.
- [49] B. Mazumber, P. Chirico, A. L. Hector, *Inorg. Chem.* **2008**, 47, 9684–9690.
- [50] D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, 115, 278–309; *Angew. Chem. Int. Ed.* **2003**, 42, 268–297.
- [51] M. H. Zeng, M. X. Yao, H. Liang, W. X. Zhang, X. M. Chen, *Angew. Chem.* **2007**, 119, 1864–1867; *Angew. Chem. Int. Ed.* **2007**, 46, 1832–1835.
- [52] R. H. Laye, E. J. L. McInnes, *Eur. J. Inorg. Chem.* **2004**, 2811–2818.

- [53] R. Savu, R. Parra, E. Joanni, B. Jancar, S. A. Elizariro, R. de Camargo, P.R. Bueno, J.A. Varela, E. Longo, M. A. Zaghete, *J. Crystal Growth* **2009**, *311*, 4102–4108.
- [54] J. Yang, J.H. Zeng, S.H. Yu, L. Yang, Y.H. Zhang, Q.T. Qian, *Chem. Mater.* **2000**, *12*, 2924–2929.
- [55] D. Ma, H. Liu, H. Yang, W. Fu, Y. Zhang, M. Yuan, P. Sun, X. Zhou, *Mater. Chem. Phys.* **2009**, *116*, 458–463.
- [56] R. Roy, *J. Solid State Chem.* **1994**, *111*, 11–17.
- [57] S. K. Park, J.H. Park, K. Y. Ko, S. Yoon, K. S. Chu, W. Kim, Y.R. Do, *Crystal Growth & Design* **2009**, *9*, 3615–3620.
- [58] S. Komarneni, R. Roy, Q.H. Li, *Mater. Res. Bull.* **1992**, *27*, 1393–1405.
- [59] R.M. Piticescu, P. Vilarnho, L.M. Popescu, R. Piticescu, *J. Europ. Ceram. Soc.* **2006**, *26*, 2945–2949.
- [60] J. Wang, Q. W. Chen, C. Zeng, B. Y. Hou, *Adv. Mater.* **2004**, *16*, 137–140.
- [61] R. H. Wentorf, Jr., *Chem. Eng.* **1961**, 177–186.
- [62] D. Han, C. Song, X. Li, *Mater. Chem. Phys.* **2009**, *116*, 41–45.
- [63] T. C. Stamatatos, D. Foguet-Albiol, S. C. Lee, C. C. Stoumpos, C. P. Raptopoulou, A. Terzis, W. Wernsdorfer, S. O. Hill, S. P. Perlepes, G. Christou, *J. Am. Chem. Soc.* **2007**, *129*, 9484–9499.
- [64] W. J. Son, J. Kim, W.-S. Ahn, *Chem. Commun.* **2008**, *47*, 6336–6338.
- [65] T. Nathan, M. Cloke, S. R. S. Prabaharan, *J. Nanomater.* **2008**, articleID 94813.
- [66] C. H. Yu, Z. H. Han, J. Yang, H. Q. Zhao, R. Y. Yang, Y. Xie, Y. T. Qian, Y. H. Zhang, *Chem. Mater.* **1999**, *11*, 192–194.
- [67] J. Lu, Y. Xie, G. Du, X. Jiang, L. Zhu, X. Wang, Y. Qian, *J. Mater. Chem.* **2002**, *12*, 103–106.
- [68] S. Huaqiang, Z. Xiaodong, X. Fu, W. Debao, H. Zhengsdai, *Mater. Lett.* **2006**, *60*, 1793–1795.
- [69] M. Wen, H. Qi, W. Zhao, J. Chen, L. Li, Q. Wu, *Colloids and Surfaces: Physicochem. Eng. Aspects* **2008**, *312*, 73–78.
- [70] S. Yang, L. Gao, *Mater. Chem. Phys.* **2006**, *99*, 437–440.
- [71] J. Liu, J. Ma, Y. Liu, Z. Song, Y. Sung, J. Fang, Z. Liu, *J. Alloys & Compd.* **2009**, *486*, L40–L43.
- [72] K. Li, H. H. Jiang, G. Lian, Q. L. Wang, X. Zhao, D. L. Cui, X. T. Tao, *Chin. Sci. Bull.* **2007**, *52*, 1785–1790.
- [73] G. Demazeau, *J. Mater. Sci.* **2008**, *43*, 2104–2114.
- [74] G. Zhu, P. Liu, *Cryst. Res. Technol.* **2009**, *44*, 713–720.
- [75] U. Sulaeman, S. Yin, T. Suehiro, T. Sato, *IOP Conf. Series: Mater. Sci. Eng.* **2009**, *1*, 012017 (11 pages).
- [76] J. Sheng, K. Tang, Z. Liang, Y. Wang, D. Wang, W. Zhang, *Mater. Chem. Phys.* **2009**, *115*, 483–487.
- [77] A. Y. Jee, M. Lee, *Carbon* **2009**, *47*, 2546–2548.
- [78] W. Zhang, D. Ma, J. Liu, L. Kong, W. Yu, Y. Qian, *Carbon* **2004**, *42*, 2341–2343.
- [79] W. Qian, R. Hao, Y. Hou, Y. Tian, C. Schen, H. Gao, X. Liang, *Nano Research* **2009**, *2*, 706–71.
- [80] R. E. Morris, *Chem. Commun.* **2009**, 2990–2998.
- [81] W. S. Dong, F. Q. Lin, C. L. Liu, M. Y. Li, *J. Colloid Interf. Sci.* **2009**, *333*, 734–740.
- [82] Y. C. Zhang, G. Y. Wang, K. Y. Hu, R. Xing, *J. Solid State Chem.* **2005**, *178*, 1609–1613.
- [83] G. Seeta Rama Raju, H. C. Jung, J. Y. Park, C. M. Kanamadi, B. K. Moon, J. H. Jeong, S.-M. Son, J. H. Kim, *J. Alloys & Compd.* **2009**, *481*, 730–734.
- [84] P. Yang, Z. Quan, C. Li, Z. Hou, W. Wang, J. Lin, *J. Solid State Chem.* **2009**, *182*, 1045–1054.
- [85] T. Huang, L. Qi, *Nanotech.* **2009**, *20*, 25606.
- [86] S. Sun, Z. Zou, G. Min, *Mater. Chem. Phys.* **2009**, *114*, 884–888.
- [87] B. H. Xu, B. Z. Lin, Z. J. Chen, X. L. Li, Q. Q. Wang, *J. Colloid Interf. Sci.* **2009**, *330*, 220–226.
- [88] Q. Zhang, M. Zhu, Q. Zhang, Y. Li, H. Wang, *Mater. Chem. Phys.* **2009**, *116*, 658–662.
- [89] N. G. Holm, E. Andersson, *Astrobiol.* **2005**, *5*, 444–460.
- [90] J. S. Seewald, M. Yu Zolotov, T. McCollom, *Geochim. Cosmochim. Acta* **2006**, *70*, 446–460.
- [91] A. D. Aubrey, H. J. Cleaves, J. L. Bada, *Origins of Life and Evolution of the Biosphere: The Journal of the International Society for the Study of the Origin of Life* **2009**, *39*, 91–108.
- [92] S. Feng, G. Tian, C. He, H. Yuan, Y. Mu, Y. Wang, L. Wang, *J. Mater. Sci.* **2008**, *43*, 2418–2425.
- [93] T. Mahenthirajah, Y. Li, Ph. Lightfoot, *J. Solid State Chem.* **2009**, *182*, 3125–3130.
- [94] S. Sharma, S. Komarneni, *Appl. Clay Sci.* **2009**, *42*, 553–558.
- [95] D. Ehrentraut, Y. Kagamitani, C. Yokoyama, T. Fukuda, *J. Crystal Growth* **2008**, *310*, 891–895.
- [96] T. Hashimoto, F. Wu, J. S. Speck, S. Nakamura, *J. Crystal Growth* **2008**, *310*, 3907–3910.
- [97] L. N. Demyanets, V. I. Lyutin, *J. Crystal Growth* **2008**, *310*, 993–999.
- [98] C. L. Zhang, W. N. Zhou, Y. Hang, Z. Lu, H. D. Hou, Y. B. Zuo, S. J. Qin, F. H. Lu, S. L. Gu, *J. Crystal Growth* **2008**, *310*, 1819–1822.
- [99] J. Ma, X. Liu, L. Wu, W. Zheng, *Cryst. Res. Technol.* **2008**, *12*, 1297–1299.
- [100] F. Lin, G. Q. Bian, Z. X. Lei, Z. J. Lu, J. Dai, *Solid State Sci.* **2009**, *11*, 972–975.
- [101] Th. Fischer, H. Hess, *J. Mater. Chem.* **2007**, *17*, 943–951.