Hydrothermal/Solvothermal Processing of Advanced Ceramic Materials

先進セラミックス材料におけるハイドロサーマル/ソルボサーマルプロセス

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Ceramic materials/nanomaterials have received considerable interests and attention in materials science due to their potential applications such as to electronics, optics, catalysis, and magnetic storage. From the viewpoint of applications, it is very important to process ceramic materials with well-defined shapes, sizes, and form. However, most ceramic materials processing methods such as solid state reactions, CVD, MOCVD, and PVD involved using higher temperatures, or toxic organometallic precursors, or complicated reaction and post-treatment systems. Exploration of novel, convenient, lower temperature, and environmentally friendly solution processing routes for synthesis of advanced ceramic materials with desired shapes and sizes has been challenged in materials science. This review focuses on the latest development of hydrothermal process, its integration with other activation methods such as electrochemistry, microwave, and its counterpart solvothermal process for fabrication of ceramic thin films, nanoparticles, and single crystals. Especially, as a new emerging process and one complement for conventional hydrothermal process, solvothermal process has proved to play a significant role in synthesis of advanced non-oxide ceramic materials by using reactions in non-aqueous solutions, which will be an exciting and promising field for preparation of ceramic materials. Shapes, sizes, and phases of the synthesized ceramics are expected to be well controlled by employing different solution processes, which will play a key role in tailoring the properties of ceramic materials. These new innovations in hydrothermal/solvothermal processing may find wide applications in rational design of advanced ceramic materials in future.

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1. Introduction

ADVANCED inorganic materials/nanomaterials have received considerable interests and attention in scientific research due to their potential applications¹⁾ such as to electronics,²⁾ optics,³⁾ catalysis,⁴⁾ ceramics,⁵⁾ and magnetic storage.⁶⁾ From the viewpoint of applications, it is very important to process ceramic materials with well-defined shapes, sizes, and form. Nanostructured materials with the size of 1–100 nm display optical, electronic, and structural properties that often are not present in either isolated molecules or macroscopic solids. Well-defined ordered solids prepared from tailored nanocrystalline building blocks provide opportunities for optimizing properties of materials and offer possibilities for observing interesting and potentially useful new collective physical phenomena. For example, the theoretical prediction^{7),8)} that semiconductor band gaps should increase as the dimensionality of the material grows smaller has been investigated in luminescence⁹⁾ and other spectroscopic studies.^{10),11)}

Conventional solid state reaction route for inorganic materials synthesis needs higher temperatures ($\sim 1000^\circ\text{C}$).¹²⁾ More recent ceramic materials processing methods such as chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD),^{13),14)} and physical vapor deposition (PVD)¹³⁾ involved using a gaseous phase and vacuum system. Generally, processing of materials consists of two steps: (1) synthesis of substances which possess particular chemical composition and physical state; and (2) materials fabrication (shape-forming and shape-fixing) by firing/sintering, pyrolysis, melting and casting. This two-step processing method usually requires high tempera-

tures, or using toxic organometallic precursors, or complicated reaction and post-treatment systems, therefore, it will consume a lot of energy¹⁵⁾ and put stresses on the environment.¹⁶⁾ Especially, it has been a daunting task to give inorganic materials desired shapes, sizes, and forms due to their brittleness.¹⁷⁾ In contrast, recent development in solution-based processing may provide an alternative, convenient, lower temperature, and environmentally friendly pathway for fabrication of advanced ceramic materials with desirable shapes and sizes.

It is well known that hydrothermal process has been widely used to prepare ceramics materials at elevated temperatures ($> 80^\circ\text{C}$) and pressure ($> 1 \times 10^5$ Pa). In recent years, hydrothermal processing of materials has aroused broad attention due to its versatility and low energy consumption, which have been demonstrated in synthesis, crystal growth, treatment, fabrication, alteration, hot pressing, recycling, sintering, etc.¹⁸⁾ As the counterpart of hydrothermal process, solvothermal process has emerged in recent years and has received great attention in synthetic chemistry and materials science.

Hydrothermal/solvothermal processing of materials can be included in a recent new concept which termed as soft solution processing (SSP) proposed by Yoshimura.^{16),19),20)} Soft solution processing has a broad meaning, and it covers only a portion of the hydrothermal research and refers mainly to any solution processing at or near the ambient conditions. Soft solution-processing of inorganic materials has several advantages over traditional solid state reactions. First, many inorganic materials can be prepared at substantially lower temperatures than solid state reactions. Shorter diffusion distances for reactants lead to lower temperatures for crystallization which, in turn, alleviate stoichiometry problems associated with volatilization of high vapor pres-

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sure components.^{16),19),20)}

Second, it provides a versatile technique for fabrication shaped/sized/oriented ceramics in solution via only one step, without firing/sintering or melting,^{16),19),20)} or without the need to use powders.²¹⁾ Thirdly, the solution nature of the process offers molecular level mixing of constituents leading to excellent chemical homogeneity and composition control, particularly important features for multi-component systems.²¹⁾ Soft solution processing requires simple equipment, low temperatures, and seems to be the most environmentally friendly and the lowest energy consumption process among existing processing routes for ceramic materials. It allows us to prepare unique materials with unique properties. Moreover, morphology and chemical composition of the synthesized ceramics could be easily controlled by adjusting processing conditions.^{16),19),20)}

In the following parts, the latest development and progress on novel innovations of hydrothermal/solvothermal processing of advanced ceramic materials are discussed with focus on new emerging solvothermal processing of ceramic materials.

2. New trends for hydrothermal/solvothermal processing of advanced inorganic materials

2.1 Hydrothermal processing

Hydrothermal processing of materials has been becoming a popular research field particularly after the successful development of ceramic processing technology during 1970s. In order to enhance the hydrothermal reaction kinetics and prepare non-oxide materials, several novel innovations of the hydrothermal conditions to prepare powders and thin films have emerged²²⁾ such as hydrothermal-electrochemical method,^{16),19),20)} microwave-hydrothermal method.²²⁾ In addition, other innovations include introducing ultrasonic energy, sonochemical simulation, ionizing and nonionizing radiation, mechanical mixing into hydrothermal process.²²⁾ The following parts only focus on the development of hydrothermal-electrochemical method and microwave-hydrothermal method and their innovations.

2.1.1 Hydrothermal-electrochemical method and its flowing system for fabrication of ceramic thin films

Low temperature, *in situ* fabrication of crystalline, thin films is essential to improve their quality, lower costs, and make the whole process environmentally friendly. It has been accomplished by Yoshimura's group via introducing hydrothermal and/or electrochemical methods to film preparation.^{19),20)} These techniques allow various double oxide films to be prepared on substrates such as metal, alloy, or oxide. The substrate works as an electrode which reacts chemically and/or electrochemically (by passing electrical current) with cation components of the surrounding solution. This processing route may involve the following reactions:²⁰⁾ (a) hydrothermal reaction between anodically oxidized film with solution components, (b) electrochemical reaction with solution components, (c) electrolytic oxidation of dissolved species and hydrothermal reaction, (d) hydrothermal reaction between anodically dissolved species and solution components, (e) electro-discharge reaction between anodic oxidized film with solution components, and (f) electro-deposition of charged oxide particles.

This method has the feature of making positive use of the reaction between the electrolytic solution and the electrode under hydrothermal conditions at relatively low temperature (100–200°C). It has been proved that it is possible to fabricate crystalline, complex oxides *in situ* on the substrate.^{19),20)} Other advantages include relatively high growth rate of the films (up to several microns per hour)

and low fabrication temperature. Several advanced ceramic materials have been synthesized by these techniques such as BaTiO₃,²³⁾ SrTiO₃,^{24)–29)} SrTiO₃-BaTiO₃,^{30),31)} CaTiO₃,³²⁾ BaFeO₄(BaTiO_{3-x}), LiNbO₃,³³⁾ PbTiO₃,³⁴⁾ and LiNiO₂.³⁵⁾ have been prepared on various substrates (metals, oxides, and alloys) by the hydrothermal and/or hydrothermal electrochemical method at temperatures rarely exceeding 200 °C. Recent work shows spinel ferrite/metal composite thin films of MFe₂O₄/Fe (M = Zn, Mg) with controlled grain sizes and shape were directly fabricated by a soft solution-processing route in which involved the liquid-solid interfacial hydrothermal reaction of Fe substrate with metal ions M²⁺ (M = Zn, Mg) in ammonia solution at lower temperatures (<200°C).³⁶⁾ Figure 1 shows the typical SEM images of ZnFe₂O₄ and MgFe₂O₄ thin films fabricated on Fe substrate. The saturation magnetization of the ferrite/Fe composites thin films was found to be much improved compared with that of single phase ferrite products, and the ferrite/Fe thin films displayed unusual superparamagnetism.³⁶⁾

Especially, a solution flow system for hydrothermal-electrochemical synthesis of ceramic thin films has been successfully constructed and its intergrations with electro- or photo-activation allow the fabrication of multilayered materials in one experiment simply by alternatively changing the flowing solutions.³⁷⁾ A general schematic of the flowing cell is shown in Fig. 2. Another important feature of this flow-cell system is the possibility in solution recycling in a closed-flow system during the synthesis will minimize the cost of the process and its environmental effects.

2.1.2 Microwave-hydrothermal method for synthesis of ceramic powders

Since significant rate acceleration for reactions carried out in a conventional microwave oven was observed in 1986,^{38),39)} there have been considerable increasing attention on reactions carried out while subject to dielectric heating.⁴⁰⁾ Microwaves are widely used in today's materials processing technology.^{41)–43)} Microwave heating provides the following properties:^{40),41),43)} (a) volumetric heating rather than the surface absorption and thermal diffusion afforded by conventional heating; (b) potentially "uniform" heat distribution; (c) rapid heating rates, and (d) the possibility of selectively heating desired materials. Microwave processing of solid-state materials is widely studied.^{44),45)} The common practice use of microwaves in analytical chemistry is to dissolve inorganic and organic samples for chemical analysis.⁴⁶⁾ During the last several years, a few groups have shown that chemical syntheses in solutions may be significantly accelerated using microwave through dielectric heating effects. The microwave-assisted synthesis method has been shown to be applicable to organic reaction,^{47)–49)} organometallic syntheses,⁵⁰⁾ synthesis of intercalation compounds,⁵¹⁾ and preparation of inorganic zeo-

Fig. 1. SEM images for as prepared ZnFe₂O₄/Fe and MgFe₂O₄/Fe composite films prepared in 29% ammonia solution at 180°C for 12 h: (a) ZnFe₂O₄/Fe, [Zn²⁺] = 0.5 M; (b) MgFe₂O₄/Fe, [Mg²⁺] = 0.01 M.

Fig. 2. General schematic of the flow cell for hydrothermal-electrochemical synthesis.

lites and molecular sieves.⁵²⁾

Komarneni et al. introduced microwave field into hydrothermal method to synthesize a wide range of ceramic powders^{53)–58)} which has been named as the microwave-hydrothermal method. The main advantages of the microwave-hydrothermal method over conventional hydrothermal methods in powders synthesis are (i) the kinetics of reaction are increased by one to two orders of magnitude,^{53),56)} (ii) novel phases are formed,^{48),49)} and (iii) the initial heating is rapid which can lead to energy savings.⁵⁸⁾ In addition to the synthesis of ceramic oxide powders, the microwave-hydrothermal method has been used to prepare metal-intercalated clay nanocomposites,^{55),59)} metal powders,⁵⁷⁾ and silica gels.⁶⁰⁾ A recent study by Komarneni et al.⁴²⁾ shows that the formation of metal powders such as Cu, Ni, Co, and Ag is also very rapid (~15 min) compared to the conventional polyol process which needs several hours. Also, the kinetics of metal crystallization is enhanced by microwave. The acceleration of inorganic synthesis has also been reported recently.^{60)–62)} However, the reaction mechanism is still not so clear and need to be investigated further.

2.2 Solvothermal processing

2.2.1 Solvothermal process: an emerging mild route in synthetic chemistry

Recently, researchers proposed a future in which conventional solid-state reactions will be conducted in round-bottom flasks or by solution-based chemical processes.^{12),63)} Ideally, the reaction conditions will be mild and the strategies will be more akin to those of organic chemists than to the high-temperature methods presently employed.⁶³⁾ As one kind of solution-based chemical processes, hydrothermal process has been widely used for the synthesis of vast range of solid-state compounds such as oxides, sulfides and halides,^{64)–66)} since the pioneering work from 1960s to 1980s.

In recent years, the concepts embodied in hydrothermal process have been extrapolated to non-aqueous system, therefore, its counterpart so-called "solvothermal process" emerges, in which organic solvents were used as reaction

media instead of water as reaction media. Several reasons stimulated research into solvothermal synthetic method: First, technological interest in the design of solid-state phases with tailor-made properties has stimulated research into solid-state synthetic methods at intermediate temperatures (100–600°C), including molten flux and solvothermal techniques, both of which involves solubilitization of inorganic starting materials.⁶⁷⁾ As an alternative to solid-state reaction at temperature (typically > 600°C) higher enough to allow adequate diffusion of atoms or ions to the site of product formation, solvothermal technique removes diffusion control by use of a suitable solvent and restricts the reaction to one or more functional groups and leaves the majority of the chemical bonds intact by employment of relatively low temperature.⁶⁷⁾ Second, conventional hydrothermal method is confined under conditions that some reactants will decompose in the existence of water or the precursors are very sensitive to water, or some reactions will not happen while water exists, resulting in the failure in synthesis of the desired compounds. Therefore, it is difficult to obtain many kinds of powders, such as carbonides, nitrides, phosphides, silicides, chalcogenides, and so on by conventional hydrothermal process. Thus, by substitution of non-aqueous solvents (both polar and apolar solvents) such as alcohols, C₆H₆, polyamines, NH₂NH₂, liquid NH₃ for water, solvothermal process has been developed to prepare various nanocrystalline compounds and to initiate some conventional solid-state reactions in organic media under mild conditions.

In solvothermal process, one or several kinds of precursors are dissolved in non-aqueous solvents. The reactants are dispersed in solution and become more active. The reactions happen in liquid phase or supercritical status. Solvothermal process is relatively simple and easy to control with several changeable parameters such as solvents, temperature, and reaction time. The sealed system can effectively prevent the contamination of the toxic and air-sensitive precursors. By substitution of non-aqueous solvents such as polar and non-polar solvents for water, the so-called solvothermal process can be widely extended to prepare various kinds of non-oxide nanocrystalline materials whose precursors are very sensitive to water.

In fact, solvothermal synthesis may be regarded as a special case of chemical transport reaction.⁶⁸⁾ The potential of this technique for preparative solid-state chemistry was reviewed by Rabenau,⁶⁴⁾ Sheldrick,⁶⁷⁾ and Demazeau.⁶⁹⁾ Morris and Weigel⁷⁰⁾ summarized some of the results of the recent works in the synthesis of molecular sieves from non-aqueous solvents. In 1985, Bibby and Dale reported the first example of the synthesis of silica-sodalite from ethylene glycol and propanol solvents, a novel compound which can not be prepared from an aqueous system.⁷¹⁾ Since then, non-aqueous synthesis technique is extended to synthesize zeolite,^{72)–74)} and aluminophosphates.^{75),76)} Oliver et al.⁷⁷⁾ reported a synthesis procedure for lamellar aluminophosphates with surface patterns that mimic diatom and radiolarian microskeletons by a solvothermal treatment of a mixture with composition of 14TEG:0.9Al₂O₃:2.5H₂O:1.8P₂O₅:3.0C₁₀H₂₁NH₂ using non-aqueous tetraethylene glycol (TEG) as solvent.

Various oxide ceramic ultrafine powders were prepared by solvothermal process. Fanelli and Burlew reported the synthesis of fine-particle-size transition alumina by the treatment of aluminum *sec*-butoxide in *sec*-butyl alcohol.⁷⁸⁾ Metallic powders such as cobalt, nickel, and copper were synthesized by reduction of inorganic compounds in ethylene glycol.⁷⁹⁾ Inoue et al. reported the synthesis of inorganic materials in organic media at elevated temperatures (200–300°C) under autogenous pressure of organics.^{80)–84)} They demonstrated that some oxides such as α -Al₂O₃ and

yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) can be synthesized in organic media at lower temperatures (250, 300°C, respectively) than in water by hydrothermal reaction (>450°C, 350–600°C, respectively).^{81,82} Demazeau et al. reported the synthesis of Fe_2O_3 ⁸⁵ and CeO_2 ⁸⁶ fine powders using alcohol as solvent by solvothermal process. A solvothermal treatment of a gel prepared from $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9)_3$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$ using 2-methoxyethanol as solvent produced a new class of bidimensional oxides $\text{K}(\text{Mg}_2\text{Al})\text{Si}_4\text{O}_{12}$ ($50 < P < 100$ MPa, $700 < T < 800^\circ\text{C}$, $48 < t < 72$ h).⁶⁹

Now, a trend to considerably milder conditions (100–200°C) has become increasing apparent over the past two decades for the inorganic synthesis chemistry and materials synthesis.⁶⁷ Sheldrick and his co-workers successfully synthesized solid-state chalcogenidometates by solvothermal synthesis technique.⁶⁷ They also obtained many novel solid-state compounds such as a new class of very tellurium rich alkali metal tellurides such as RbTe_6 and Cs_3Te_2 ,⁸⁷ and metastable compounds such as $\text{Cs}_4\text{Te}_{28}$.⁸⁸ Different solvothermal processes for synthesis of non-oxides materials with special shape, phases, and sizes will be discussed in following parts.

2.2.2 Solvothermal processing of advanced non-oxide nanomaterials and single crystal: shape, sizes, and phase control—adding new variables in tailoring the properties of materials

Nanometer-size inorganic dots, tubes, and wires exhibit a wide range of electronic and optical properties that depend sensitively on both size and shape, and are of both fundamental and technological interest.^{89,90} Currently, a lot of efforts have been made for synthesis of technologically important semiconductors from the group II–VI, III–VI, and IV families of materials. Especially, the ability to control the shapes of semiconductor nanocrystals affords an opportunity to further test theories of quantum confinement, and yields samples with desirable optical characteristics from the viewpoint of application.⁹¹ Recently, manipulation of the shapes of II–VI semiconductor CdSe nanoparticles has been highlighted.⁹² Although several examples have been demonstrated, shape control has been more difficult to achieve. A challenge in materials science in future is to control not only the particle sizes but also their shapes, which will add alternative variable in tailoring the properties of materials. Figure 3 shows a schematic illustration of the preparation of semiconductor nanocrystals with ideal shapes and sizes, and the relationship of the band gap with the nanoparticle sizes.

Fig. 3. Schematic illustration of the preparation of semiconductor nanocrystals with ideal shapes and sizes, and the relationship of the band gap with the nanoparticle sizes.

Solvothermal extension of the temperature and solubility ranges in which to conduct solution-phase syntheses may lead to important discoveries in metastable semiconductor structures. Solvothermal growth of crystalline group IV Si and Ge crystals have been successfully demonstrated by Health et al.^{93,94} Korgel et al. reported a supercritical fluid solution-phase self-assembly approach for growing bulk quantities of defect-free Si nanowires with nearly uniform diameters ranging from 4–5 nm and a length of several micrometers, using alkanethiol-coated gold nanocrystals (2.5 nm) as uniform seeds to direct one-dimensional Si crystallization in supercritical hexane at 500°C and 270 bar.⁹⁵

In recent years, our group has been devoted to exploring mild solution routes for synthesis of non-oxide compounds such as metal chalcogenides, metal nitrides, and phosphides,^{96–106,110–120} especially, we explored controllable fabrication of semiconductor nanocrystalline with different sizes and shapes by solvothermal process. Our results showed that the physico-chemical properties of the solvents have strong effects on the reaction activity, shapes, sizes, and phases of the particles, since solvent properties such as polarity, viscosity, and softness will strongly influence the solubility and transport behavior of the precursors under solvothermal conditions.

2.2.2.1 Synthesis of metal nitride materials

Nanocrystalline GaN was successfully synthesized by a benzene-thermal route at near temperature near 300°C, importantly, a small amount of metastable rocksalt-phase GaN was found, which was only observed under ultrahigh pressure of at least 37 GPa before.⁹⁶ The liquid-solid reaction under solvothermal conditions reaction can be expressed as Eq. (1)

Other metal nitrides can also be synthesized by a similar process, for example, nanocrystalline TiN with average grain size of about 50 nm was synthesized via following reaction in benzene media at 350–380°C:⁹⁷

Compared with other synthetic methods, solvothermal process provides with a relative mild pathway for synthesis of metal nitrides materials. Especially, recent work by Demazeau et al.⁶⁹ indicated that a new nitride graphitic structure C_3N_4 can be synthesized by either condensation of melamine (2,4,6-triamino-1,3,5-triazine) and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) at 250°C and 130 MPa in triethylamine solvent or the thermolysis of melamine $\text{C}_3\text{N}_6\text{H}_6$ at high pressure 2.5–3 GPa in the temperature range of 800–850°C using hydrazine NH_2NH_2 as the nitriding solvent.

2.2.2.2 Synthesis of metal chalcogenides and their shapes, sizes, and phases control

Recently, we found that a novel solvothermal reaction between metal oxalates and chalcogens in organic media under mild conditions (120–200°C) can produce various metal chalcogenide semiconductors such as CdE ,⁹⁸ PbE , Bi_2E_3 ,⁹⁹ Ag_2E ,¹⁰⁰ NiE_n ,¹⁰¹ SnE ,¹⁰² Cu_xE ($\text{E} = \text{S}, \text{Se}, \text{Te}$),¹⁰³ and other transition metal chalcogenides with high yields. The reaction can be formulated as:

Table 1 lists the detained experimental conditions for synthesis of various metal chalcogenides materials by solvothermal reaction between metal oxalates and chalcogens, and the characterization of the powders. As shown in the table, the solvothermal reactions in ethylenediamine (en) proceed more completely than in other solvents such as pyri-

Table 1. Summary of Various Metal Chalcogenides Synthesized by Solvothermal Process, Including Experimental Conditions such as Reactants and Molar Ratio (M/E) (M=Metal Source, E=S, Se, Te), Solvent, Temperature and Time; the Detected Phases by X-ray Powder Diffraction, Symmetry, and the Particle Shape

Reactants (M/E ratio)	Solvent	Reaction conditions	Phase	Symmetry	Shape
CdC ₂ O ₄ + S(2:1)	en	120-180°C, 12h	CdS	hexagonal	rod-like
CdC ₂ O ₄ + S(2:1)	py	160-180°C, 12h	CdS	hexagonal	spherical
CdC ₂ O ₄ + S(2:1)	EG	160-180°C, 12h	CdS	hexagonal	spherical
CdC ₂ O ₄ + Se(2:1)	en	140°C, 12h	CdSe	hexagonal	rod-like
CdC ₂ O ₄ + Se(2:1)	py	160°C, 12h	CdSe	hexagonal	spherical
CdC ₂ O ₄ + Se(2:1)	py	140°C, 12h	Se + CdSe*		
CdC ₂ O ₄ + Te(2:1)	en	180°C, 12h	CdTe	cubic	rod-like
PbC ₂ O ₄ + S(1:1)	en	120°C, 12h	PbS	cubic	square
PbC ₂ O ₄ + S(1:1)	py	120°C, 12h	PbS	cubic	square
PbC ₂ O ₄ + Se(1:1)	en	160°C, 12h	PbSe	cubic	square
PbC ₂ O ₄ + Se (1:1)	py	160°C, 12h	PbSe + Se*		
PbC ₂ O ₄ + Te(1:1)	en	160°C, 12h	PbTe	cubic	square
PbC ₂ O ₄ + Se(1:1)	py	160°C, 12h	PbTe + Te*		
SnC ₂ O ₄ + S(1:1.2)	en	240°C, 8h	SnS	orthorhombic	plate-like
SnC ₂ O ₄ + Se(1:1.2)	en	180°C, 8h	SnSe	orthorhombic	rod-like
SnC ₂ O ₄ + Te(1:1.2)	en	170°C, 8h	SnTe	cubic	spherical
Ag ₂ C ₂ O ₄ + S(1:1)	en	140°C, 12h	Ag ₂ S	monoclinic	spherical
Ag ₂ C ₂ O ₄ + S(1:1)	py	140°C, 12h	Ag ₂ S	monoclinic	spherical
Ag ₂ C ₂ O ₄ + S(1:1)	THF	140°C, 12h	Ag ₂ S	monoclinic	spherical
Ag ₂ C ₂ O ₄ + Se(1:1)	en	140°C, 12h	Ag ₂ Se	orthorhombic	plate-like
Ag ₂ C ₂ O ₄ + Se(1:1)	py	140°C, 12h	Ag ₂ Se + Se*		
Ag ₂ C ₂ O ₄ + Se(1:1)	py	160°C, 12h	Ag ₂ Se + Ag*		
Ag ₂ C ₂ O ₄ + Se(1:1)	THF	140°C, 12h	Ag ₂ Se + Se*		
Ag ₂ C ₂ O ₄ + Te(1:1)	en	180°C, 12h	Ag ₂ Te + Se*	monoclinic	
Ag ₂ C ₂ O ₄ + Te(1:1)	en	160°C, 12h	Ag + Ag ₂ Te*		
Ag ₂ C ₂ O ₄ + Te(1:1)	py	180°C, 12h	Ag + Ag ₂ Te*		
Ag ₂ C ₂ O ₄ + Te(1:1)	THF	180°C, 12h	Ag + Ag ₂ Te*		
Bi ₂ (C ₂ O ₄) ₃ + Se(1:1)	en	140°C, 12h	Bi ₂ Se ₃	rhombohedral	plate-like
Bi ₂ (C ₂ O ₄) ₃ + Se(1:1)	py	140°C, 12h	Bi ₂ Se ₃ + Se*		
NiC ₂ O ₄ · 2H ₂ O + Se(1:2.4)	en	170°C, 8h	NiSe ₂	cubic	octahedral
NiC ₂ O ₄ · 2H ₂ O + Se(1:1)	en	200°C, 8h	Ni _{0.85} Se	hexagonal	starfish-like
NiC ₂ O ₄ · 2H ₂ O + Se(3:2)	en	220°C, 8h	Ni ₃ Se ₂	triclinic	dendritic
NiC ₂ O ₄ · 2H ₂ O + Se(1:1)	en	180°C, 8h	NiSe ₂	cubic	spherical
NiC ₂ O ₄ · 2H ₂ O + Se(1:2.2)	py	180°C, 8h	NiSe ₂	cubic	octahedral
NiC ₂ O ₄ · 2H ₂ O + Se(1:2.2)	THF	170°C, 8h	NiSe ₂	cubic	octahedral

Note: en-ethylenediamine; py-pyridine; THF-tetrahydrofuran; * indicates the dominant phase in the sample.

dine (py) and tetrahydrofuran (THF), suggesting that the higher reactivity in en can be achieved compared with other solvents. Both solvent and temperature play key roles in the reaction, shapes, sizes, and phases. Especially, solvent has a significant effect on the morphology of the particles as shown in Table 1.

We found that polyamines such as ethylenediamine (en), diethylenetriamine (dien), and triethylenetetraamine (trien), which have more than two N-chelating atoms, can be used as "shape-controller" of nanoparticles. Several kinds of materials such as CdE (E=S, Se, Te), SnSe synthesized in polyamines display rod-like morphology. TEM image Figs. 4(A) and (B) show that CdS nanocrystallites synthesized by a reaction of CdC₂O₄ with S in en at 160°C are uniform nanorods with diameters of 20–50 nm and lengths of 200–1300 nm, in contrast, the particles obtained in pyridine under the same conditions display spherical disc-like

shape with a size of 40 nm. Similarly, CdSe, CdTe, and CdS_xSe_{1-x} nanorods or nanowires can also be obtained by similar process.^{98),104)}

In addition, other modified solvothermal reactions as expressed in Eqs. (4) and (5) were also used to synthesize CdS nanoparticles with different morphology, particle sizes, and phases.^{105),106)}

Figures 5(a) and (b) indicated that the widths of CdS nanorods increased with increasing temperature. As-prepared CdS nanorods show [001] preferential orientation as shown in a typical HRTEM image in Fig. 5(c), corresponding to stronger and sharper 002 diffraction peak in XRD pattern. SEAD inserted in Fig. 5(c) indicated the CdS

Fig. 4. TEM images of (a) CdS nanorods synthesized by a solvothermal reaction of CdC_2O_4 with S in ethylenediamine at 160°C for 12 h. (b) disc-like CdS nanoparticles synthesized in pyridine at 120°C for 12 h.

nanorods are polycrystalline with wurtzite structure. As further results, single crystal CdS nanorods can also be obtained.

UV-absorption spectrum in Fig. 6 shows that the absorption onset of CdS nanorods obtained at 180°C blue-shifted to 480 nm (2.58 eV) compared with the bulk band gap for hexagonal macrocrystalline CdS 515 nm (2.41 eV), whereas the absorption onset of CdS nanorods obtained at 120°C blue-shifted to 435 nm (2.85 eV) besides a second well-defined peak at 374 nm (3.32 eV), which suggests the presence of a narrow cluster size distribution allows the observation of this spectral feature.^{107)–109)} This observation was sometimes taken to suggest a highly monodispersed sample of quantum dots in which evidence for excitonic recombination is observed for the first (close to band edge) and second higher energy exciton in relatively strongly quantized CdS clusters.^{107)–109)}

The special shape forming of CdS nanorods may be relat-

Fig. 6. UV-visible absorption spectrum of CdS nanorods synthesized by a solvothermal reaction of Cd^{2+} with thiourea in ethylenediamine (a) at 100°C for 12 h; (b) 180°C for 12 h.

ed to the strong N-chelating effect of bidentate ligand ethylenediamine with Cd^{2+} and its stronger hydrogen bonding action effect of the protophilic properties among molecules. Our recent results suggest that the formation of CdS nanorods synthesized by the reaction in Eq. (4) can be divided into several steps. Firstly, cadmium nitrate and thiourea reacted to produce the lamellar CdS with many folds on it. After that, the folds on the lamellae agglomerated together. Then these folds broke into needle-like fragments, which further grew to crystallized nanorods. Further studies indicate that the dissociation of ethylenediamine molecule adsorbed on the surface of CdS results in the formation of CdS nanorods.¹¹⁰⁾ The whole formation process of CdS nanorods can be expressed as:

Firstly, Cd^{2+} ion coordinated with en molecule to form $\text{Cd}(\text{en})_3^{2+}$. Thiourea decomposed to produce S^{2-} at low temperature in the base environment. Then the reaction be-

Fig. 5. TEM and HRTEM images of CdS nanorods synthesized by a solvothermal reaction of Cd^{2+} with thiourea in ethylenediamine (a) at 100°C for 12 h; (b) 180°C for 12 h; (c) HRTEM image indicated a typical CdS nanorod with a diameter *ca.* 12 nm and well resolved (002) lattice planes, which obtained by (a). Inserted electron diffraction pattern (ED) shows that the CdS nanorods are of polycrystalline nature and can be indexed as the wurtzite structure.

tween Cd(en)_3^{2+} and S^{2-} produced CdS powder with its surface adsorbed en molecule. Meanwhile, the conformation of en molecule coordinated with Cd^{2+} changed from the *gauche*-conformation to the *trans*-conformation. However, the interaction between en molecule and Cd^{2+} on the surface of CdS was weakened when en molecule used *trans*-conformation. Therefore, this structure was destroyed at high temperature. This dissociation of en molecule from the surface of CdS resulted in the evolution process of the morphology.¹¹⁰⁾ A modified solvothermal process produced CdTe crystals with different morphologies.¹¹¹⁾ More interestingly, metastable wurtzite CdTe phase and its conversion to the stable cubic CdTe phase under mild condition were observed.¹¹¹⁾

V–VI group semiconductor Bi_2S_3 nanowires with different widths and lengths were fabricated by a solvothermal decomposition process (SDP)^{112),113)} and hydrothermal crystallization process.¹¹⁴⁾ The synthetic schematic was illustrated in Fig. 7. It is interesting to note that all products of Bi_2S_3 synthesized by so-called SDP process in ethanol, pyridine, ethylene glycol (EG), and water display wire-like morphology with different widths and lengths. Bi_2S_3 powder synthesized in ethanol at 140°C for 12 h consists of uniform nanowires with widths of 25–50 nm and lengths up to 1–3 μm as shown in Fig. 8(A). The result demonstrated that the width of Bi_2S_3 nanowires is controlled by the choice of solvent and the polar solvents are more favorable for the formation of Bi_2S_3 nanowires. The difference in the width and length of the Bi_2S_3 nanowires may be related to the different physico-chemical properties of the solvents. Solvent physico-chemical properties such as polarity, viscosity, and soft-

ness will strongly influence the solubility and transport behavior of the precursors.

Based on these results, we propose a mechanism for the formation of Bi_2S_3 nanowires. First, the strong complex action between Bi^{3+} and thiourea (Tu) lead to the formation of Bi–Tu complexes in the SDP, which prevent the production of large number of free S^{2-} in the solution and will be favorable for the formation of the nanowires. Second, the Bi–Tu complexes undergo thermal decomposition at suitable temperature for a certain period of time to produce Bi_2S_3 nanowires. The formation of Bi_2S_3 nanowires can be expressed as following:

However, hydrothermal treatment of an alkiline sol (pH = 8.0–10.0) from BiCl_3 and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ with EDTA as complexing agent produced smaller short rod-like Bi_2S_3 nanoparticles with a size of $40 \times 150 \text{ nm}$ as shown in Fig. 8 (B). The direct mixing of Bi^{3+} with free S^{2-} using EDTA as complex in aqueous solution will proceed the spontaneous nucleation and produce a large number of nuclei. Then, the nucleation is much accelerated than the growth. Therefore, only smaller particles can be produced. In contrast, the decomposition of the Bi–Tu complexes in the SDP will proceed slowly and produce a smaller number of nuclei in the solution than the direct ion exchange reaction due to the position-resistance effect of the formed Bi–Tu complexes and its relatively stable properties, which would be favorable for the oriented growth of the nanowires. Therefore, the growth stage is much accelerated than the nucleation stage, since the system can finish the nucleation stage with smaller number of nuclei. So, the decomposition process in the SDP may be more favorable for the growth of the Bi_2S_3 nanowires. The solid-liquid interactions between the formed Bi–Tu complexes and the solvent under autogeneous pressure, and the decomposition of the complexes under sealed conditions would be responsible for the formation of the Bi_2S_3 nanowires with high aspect ratios.

Sb_2S_3 powders prepared previously by the benzene-thermal reaction of anhydrous SbCl_3 with Na_2S_3 were composed of irregular particles with the average size about 150 nm.¹¹⁵⁾ Our recent work shows that Sb_2S_3 nanorods can also be obtained by SDP process using thiourea as sulfur source and methanol as reaction media.¹¹⁶⁾ Interestingly, the formation of one-dimensional Sb_2S_3 nanorods is through the spontaneous connection of adjacent particles. Since higher pressure is more favorable for the self-assembly of particles to form the neck-like connections among them and a great number of connections among nanoparticles provide more opportunities for the formation of nanorods, this transformation was confirmed to be much faster in a closed system than that in an open system, indicating that pressure also plays a key role in the formation of the nanorods.

In addition, several other metal chalcogenides and phosphides such as $\beta\text{-In}_2\text{S}_3$,¹¹⁷⁾ ZnTe ,¹¹⁸⁾ IB-VIA nonstoichiometric metal tellurides,¹¹⁹⁾ and Ni_2P ¹²⁰⁾ were also synthesized by other modified solvothermal processes.

2.2.2.3 Solvothermal growth of metal chalcogenides single crystals

Recent results demonstrated that the present solvothermal process can be employed for growth of single crystals with well defined shapes. Figure 9(a) shows a typical cubic NiS_2 single crystal with well-developed $\{101\}$ polytype with dodecahedron shape and size of $1.8 \mu\text{m}$ obtained in ethylenediamine at 200°C for 18 h. Figure. 9 (b) shows cubic NiSe_2 single crystals with perfect octahedral shape and a size of 15 nm obtained by a reaction $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ with Se in ethylenediamine.¹⁰¹⁾ A typical orthorhombic $\text{Cu}_{31}\text{S}_{16}$ sin-

Fig. 7. Schematic illustration for preparation of Bi_2S_3 nanowires with controllable sizes by solvothermal decomposition process (SDP) and hydrothermal crystallization process.

Fig. 8. TEM images of (a) Bi_2S_3 nanowires fabricated by solvothermal decomposition process at 140°C , 12 h, ethanol (eth); (b) rod-like Bi_2S_3 particles prepared by hydrothermal treatment of the sol (pH = 9.3) at 150°C for 6 h.

Fig. 9. SEM images of (a) a typical NiS₂ single crystal obtained by the reaction of Ni(NO₃)₂·6H₂O with S in ethylenediamine at 200°C for 18 h, displaying well-developed {101} polytype with dodecahedron shape and size of 1.8 μm; (b) octahedron NiSe₂ single crystals with uniform sizes of 15 μm obtained by solvothermal reaction of NiC₂O₄·2H₂O with Se in ethylenediamine at 170°C for 8 h; (c) a typical polyhedron Cu₃₁S₁₆ single crystal with a size of 30 μm obtained using CuCl, Na₂C₂O₄ and S as reactants in ethylenediamine at 180°C.

gle crystals with polyhedron shape (14 faces) and a size of 30 μm can also be obtained, as shown in Fig. 9(c), by solvothermal process at 180°C in ethylenediamine.¹⁰²⁾ In addition, the solvent and the growth habit of the crystals with different structures are believed to be responsible for these distinctive shapes. The results suggested that ethylenediamine favors the crystals mostly and gives the crystals with special perfect shapes and larger sizes. Our results suggested that solvothermal process can be used to grow large single crystals with perfect shapes and preferred sizes, which may not be able to obtain by conventional hydrothermal process. These unusual shaped single crystals may display unusual properties and find unique applications. Further studies are no doubt needed to investigate the relationship between their structures (shape, sizes, phases) and their properties.

2.2.3 Selective synthesis of rare earth compounds by using different processes

Recently, rare earth compounds have been the focus of research due to their important applications in luminescent lighting, displays, and IR windows, and catalysis.^{121)–123)} Reported pathways for synthesis of these compounds mostly involved high temperatures.

We successfully developed a new solvothermal pressure-relief (SPR) process to synthesize La₂O₂S at relatively low temperature (300°C) in ethanol media using La(NO₃)₂·*n*H₂O and thiourea as reactants.¹²⁴⁾ In contrast, the normal solvothermal and hydrothermal process can only produce LaOHCO₃ and LaOHSO₄ phases, respectively. Our results demonstrated that La₂O₂S, LaOHCO₃, and LaOHSO₄ phases can be selectively synthesized under controlled conditions. Both solvents and the process employed have significant influence on the formation of La₂O₂S. The so-called SPR process is conducted in an autoclave with a controlled relief valve. The detailed procedure for the SPR process is that when the temperature reaches a desired value, then immediately open the relief valve to conduct the produced gas out of the autoclave slowly in order to make the chemical reaction equilibrium shift toward preferred direction.

The formation mechanism for La₂O₂S and LaOHCO₃ was proposed. It is well-known that thiourea reacts with water to produce gaseous NH₃, H₂S, and CO₂:

The produced gas NH₃ will react with the crystal water in the system:

Since both CO₂ and H₂S are acidic, reactions between La(OH)₃ and them immediately occurred then the following equilibria were formed:

In case of the SPR process, with the gradual decrease of the pressure in the system, the equilibrium given in Eq. (13) is more apt to move to the right than that expressed in Eq. (12). Therefore, the final product was La₂O₂S, no LaOHCO₃ phase was detected by XRD. In contrast, if the produced gas was kept in the autoclave during the whole reaction period, the equilibrium given in Eq. (13) would be severely constrained and could hardly move toward the right, therefore, the product was highly crystallized LaOHCO₃.

Based on the reaction modes and the obtained products discussed above, we believe that a transition reaction from LaOHCO₃ to La₂O₂S most probably exist in the present SPR process as expressed in Eq. (14). The equilibrium given in Eq. (14) is also more apt to move to the right in the SPR process than in normal solvothermal process.

More detailed work on the formation process of rare earth hydroxycarbonate and hydroxysulfate under hydrothermal conditions has been reported.¹²⁵⁾ Our recent work showed that new cerium hydroxycarbonate and hydroxysulfate compounds can be synthesized by hydrothermal method in thiourea-cerium(III) nitrate and urea-cerium(III) nitrate system.^{125),126)} Hydrothermal evolution of the thiourea-cerium nitrate system was investigated in detail by using Raman spectroscopy to follow the reaction solutions at different temperatures, and using XRD, XPS, and FT-IR to

characterize the solid products. The results show that thiourea decomposes before the formation of orthorhombic CeOHCO_3 . Monoclinic CeOHSO_4 is produced after SO_4^{2-} is derived from NO_3^- and HS^- in the solution at higher temperatures.

PL spectra show that the new phase CeOHSO_4 display considerably stronger ultraviolet photoluminescence which is about 400 times that of CeOHCO_3 .¹²⁶⁾

Furthermore, both shuttle-like orthorhombic crystals and butterfly-like hexagonal CeOHCO_3 crystals can be grown by hydrothermal process at 160°C and 200°C, respectively, as shown in Fig. 10. Increasing temperature is more favorable for the formation of hexagonal phase. The phase transformation between two phases and an equilibrium may exist so that made it difficult to obtain single hexagonal phase. Both phases display ultraviolet phosphorescence with luminescent bands in the range of 365–373 nm under excitation of 300 nm. Interestingly, the shuttle-like orthorhombic crystals show stronger luminescent intensity than that of the butterfly-like hexagonal crystals.¹²⁶⁾ Monoclinic $\text{La}_{1-x}\text{Ce}_x\text{OHSO}_4$ compounds ($0 \leq x \leq 1$) were also hydrothermally synthesized at moderate temperature. The crystals grown are all flake-like in morphology and display room temperature ultraviolet luminescence. The mean dimension of the crystals turns smaller, and the luminescent intensity turns stronger following the increase of cerium content in the phosphor compounds.¹²⁷⁾ These findings demonstrate that it is possible to synthesize the target rare earth compounds selectively and controllably by employing different soft solution processes and the optical properties of these phosphors could be tunable.

3. Summary and outlook

The emerging new innovations based on hydrothermal process such as hydrothermal-electrochemical process and its flowing system, microwave-hydrothermal process, and solvothermal process have obviously widened the scope of conventional hydrothermal process and will provide a large exciting possibility for improving synthesis of well-known or synthesis of unknown materials with desirable shaped/sized/oriented ceramics in solution via only one step, without firing/sintering or melting. Importantly, solvothermal process has been proved to be a fruitful route for synthesis of various non-oxides materials with special shape, controllable sizes, and phases, which may add new variables

in tailoring the materials properties and stimulate further research into the correlation of the shape, sizes, and phases of the nanomaterials with their properties.

Although these processes have shown promising future in synthesis of materials, they are not yet well established, i.e., the chemical reactivity, reaction mechanism, and the role of solvents in the reactions are very complicated and still not clear, which no doubt need to be resolved in future. Especially, some special physical and chemical characterization techniques such as IR, Raman, NMR spectroscopy will be needed to be built to *in situ* follow the evolution of the chemical reactions.

As newcomers among the promising soft solution processing techniques, these new processes may find a wider application in inorganic synthesis chemistry and materials science in future because of their effective enhancement of the reaction kinetics, synthesizing target materials selectively, controllably, economically, and environmentally friendly.

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Fig. 10. SEM images of typical CeOHCO_3 samples: (a) orthorhombic crystals obtained at 160°C; (b) hexagonal crystals obtained at 200°C.

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