Nanophase materials by hydrothermal, microwave-hydrothermal and microwave-solvothermal methods

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Hydrothermal, microwave-hydrothermal and microwave-solvothermal methods are truly low temperature methods for the prearation of nanophase materials of different sizes and shapes. These methods save energy and are environmentally benign because the reactions take place in closed system conditions. The nanophase materials can be produced in either a batch or continuous process using the above methods. Oxide materials such as zirconia, titania and various spinel ferrites and metals such as Pt, Pd, Ag, Au, etc. of different sizes and shapes were crystallized in our laboratory using the hydrothermal, microwave-hydrothermal and microwave-solvothermal methods. The key novelty of our work is the use of microwave-assisted reactions to dramatically enhance the kinetics of crystallization by one to two orders of magnitude.

NANOPHASE materials are single solid phases where at least one dimension is in the 1–100 nm range. Nanophase materials are nothing new although the term 'nanophase' is new[1]. Nature made nanophase materials such as some clays, oxides and/or oxyhydroxides of Fe, Al, Si, etc. and magnetite in magnetotactic bacteria etc. long before man. Organic molecules in the nanometer dimension are the basis of life. Nanophase materials can be organic or inorganic and essentially of any composition. Nanophase materials have properties which are size-dependent. It is well known that magnetic materials exhibit size-dependent magnetic properties that range from ferromagnetic to paramagnetic to superparamagnetic with decreasing crystal size[2]. Melting temperature of nanophases is considerably lower than their bulk counterparts, apparently as a result of higher effective pressure in the confined system[3]. In addition, nanophase materials exhibit unique physical, chemical and mechanical properties upon consolidation as a result of the interaction of crystal atoms, atoms in the grain boundaries, etc. Because of the special properties of the nanophase materials, there is a great deal of interest in their cost-effective synthesis.

There are numerous methods of synthesis of nanophase materials. These methods can be broadly classified into (a) low temperature and (b) high temperature methods[1].

Among the low temperature techniques, chemical precipitation, mechanical attrition and replication methods have been widely used. Chemical precipitation methods include precipitation of solutions[4,5] from room temperature to 100°C, hydrothermal synthesis (> 100°C and > 1 atmosphere pressure)[6–10], inverse micelle method[11], sol–gel synthesis[12], etc. These methods are ideally suited for precise control of size and shape of nanophases. In addition, they are greener because reactions are carried out in closed systems at low temperatures and cheaper because they are less energy consuming. The main drawback with the precipitation techniques is chemical contamination in general. Mechanical attrition with high energy ball milling is also used frequently to prepare nanophase metals, alloys and oxides. The main advantage of this technique is that it is rather simple and probably energy efficient. It, however, suffers from two main disadvantages: (a) contamination from the equipment used and (b) particle size and shape control is difficult. The replication method[13–15] has been used to precipitate nanophase oxides or metals by carrying out reactions in the micropores and mesopores of either crystalline or amorphous porous materials.

The high temperature methods include (a) gas condensation (b) wire explosion and (c) liquid aerosol thermolysis. In the gas condensation method[16] metal is volatilized in inert atmosphere or reactive gas to produce nanophase metals or oxides, respectively. In the wire explosion method metal wire is melted or vaporized explosively by application of a pulsed current. The liquid aerosol thermolysis[17] involves the decomposition of aerosolized solutions at high temperatures. This method is also known as evaporative decomposition of solutions (EDS).

Among the low temperature methods, the hydrothermal method is very versatile for the synthesis of nanophase materials and has been well established. Although synthesis reactions can be carried out in a temperature range of 100° to 1000°C or more and in a pressure range of 1 atmosphere to several thousand atmospheres, most of the hydrothermal experiments are conducted below the supercritical temperature of water, i.e. 374°C. The reactions can be carried out in water or in any other solvent. When water is used as a solvent, the process is called 'hydrothermal process' and when any solvent including water or organic solvents such as methanol, ethanol,

polyol, etc. are used, the process is termed 'solvothermal process'. Thus the latter term encompasses all solvents including water. Nanophase oxides can be synthesized by the hydrothermal process and the main advantages of the hydrothermal method are[18]: (a) kinetics of reaction are greatly increased with a small increase in temperature, (b) new metastable products can be formed, (c) generally single crystals are obtained, (d) high purity products can be obtained from impure feedstocks, (e) no precipitants are needed in many cases and thus the process is cost-effective, (f) pollution is minimized because of the closed system conditions and reagents can be recycled, (g) hydroxylated clays and zeolite molecular sieves[19] cannot be synthesized by any other method.

Although the hydrothermal method is very versatile, one of the main drawbacks is slow kinetics at any given temperature. In order to increase the kinetics of crystallization, one can introduce microwave or electric or ultrasonic fields in the hydrothermal system and these combinations are termed microwave-hydrothermal[20–26], elecrochemical-hydrothermal[27,28] and ultrasonic-hydrothermal[29] methods, respectively. The focus of this paper is the synthesis of nanophase oxide phases using conventional-hydrothermal and microwave-hydrothermal processes and the synthesis of nanophase metals by solvothermal process using polyols or alcohols.

Conventional-hydrothermal experiments were carried out using cold-seal vessels where both the temperature and pressure can be controlled and Parr vessels (Parr Instrument Co., Moline, IL) where temperatures can be controlled precisely but not pressure. In the latter vessels autogeneous pressure was attained and this pressure depended on the temperature of treatment. Reactions were carried out in gold capsules or teflon liners in the cold-seal and Parr vessels, respectively. The microwave-hydrothermal and microwave-solvothermal experiments were carried out using a MARS-5 acid digestion system where reactants were treated in teflon liners. Both temperature (maximum temperature of 240°C) and/or pressure (maximum pressure of 350 psi) were precisely controlled with this system. The MARS 5 system uses 2.45 GHz frequency and has a maximum power of 1200 W. The power of this unit can be controlled from 0 to 100%. The temperature inside the vessels was measured by a fiberoptic probe using a phosphor sensor.

Conventional-hydrothermal synthesis of nanophases

Nanophase zirconia, titania and various ferrites of different sizes and shapes were crystallized using conventional hydrothermal conditions[10,30,31]. Monoclinic zirconia crystals on the order of 70 nm were crystallized by hydrothermally treating a saturated solution of zirconium oxychloride in Parr vessels at 200°C for 24 h under saturated steam conditions (Figure 1). The size, shape and type of polymorph of zirconia can be easily controlled by using different precursors and hydrothermal conditions[10,30]. Nanophase anatase and rutile polymorhs of titania were crystallized by conventional hydrothermal process using cold seal vessels under different conditions[10]. Nanorods of rutile (Figure 2) were crystallized by treating 1 M titanium oxychloride solution in Parr vessels at 100°C for 3 days[30]. Nanophase ferrites of different composition were produced by hydrothermal methods in the temperature range of 175–200°C (ref. 31). Using these nanophase ferrites, very good densification was achieved[31]. The nanophase ferrites with very high surface areas are also
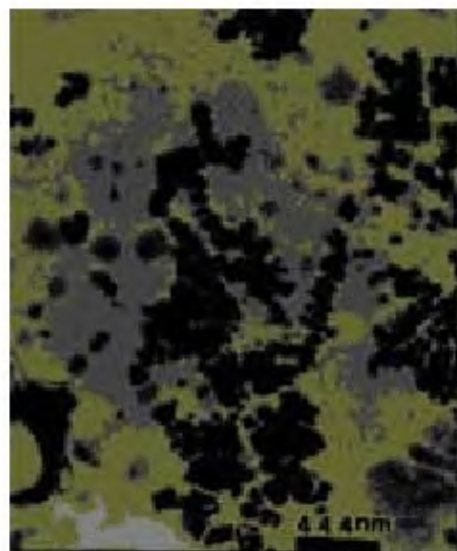

Figure 1. Transmission electron micrograph of monoclinic zirconia.

Figure 2. Transmission electron micrograph of rutile nanorods prepared by conventional-hydrothermal method.
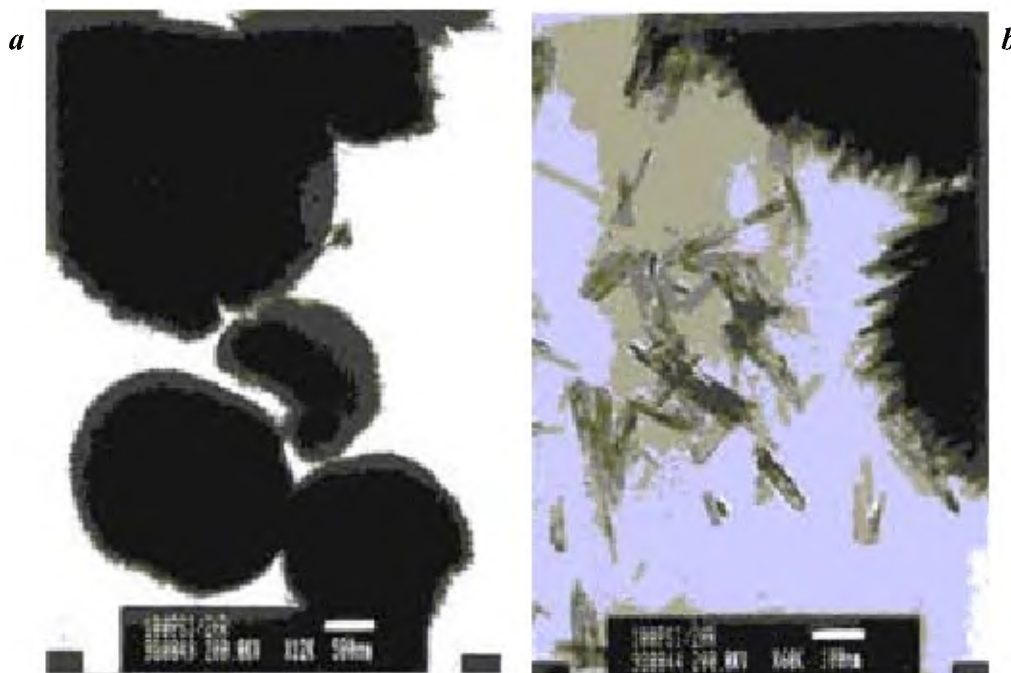
Figure 3. Crystallization under microwave-hydrothermal conditions of rutile from 2 M TiOCl₂ at about 164°C (100 psi)/2 h in the form of spheres (*a*) but the spheres show nanophase rutile rods or needles at higher magnification (*b*).
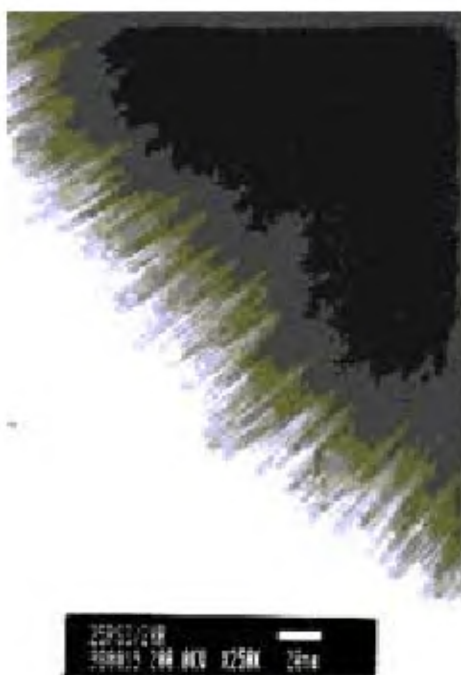

Figure 4. Crystallization from 2 M TiOCl₂ at about 116°C (25 psi)/2 h of self-assembled nanophase rutile rods or needles at the edge of a sphere under microwave-hydrothermal conditions.

candidates for CO_2 decomposition[32]. The size-dependent magnetic properties of ferrites are well known.

Microwave-hydrothermal synthesis of nanophases

As stated in the introduction, the microwave-hydrothermal method has distinct advantages over conventional hydrothermal method in the crystallization of different phases. The main advantage of microwave introduction into the reaction system is extremely rapid kinetics for synthesis. This can be exemplified by the titania crystallization under microwave-hydrothermal conditions. Rutile crystallized extremely rapidly, i.e. in 0.5 to 2 h from 0.5 to 3 M titanium oxychloride solutions[20,33] while the conventional hydrothermal method required 3 days. The extremely rapid crystallization led to large rutile spheres composed of aligned rutile nanorods of about 25 nm width and more than 100 nm in length (Figure 3) after treatment of 2 M TiOCl₂ at about 164°C/2 h. Treatment at 116°C/2 h also led to self-assembled nanorods of rutile to form spheres (Figure 4).

Nanophase ferrites of Ni, Zn, Co and Mn were synthesized under different microwave-hydrothermal conditions[26]. Figure 5 shows Ni and Mn ferrites prepared at about 164°C (100 psi) in 4 min using nitrate salts neutralized with ammonium hydroxide to a pH of about 8.7. Nanophase barium titanate was also crystallized under different conditions[34]. Spherical nanophase Ba titanate crystallized at 160°C in KOH is shown in Figure 6.
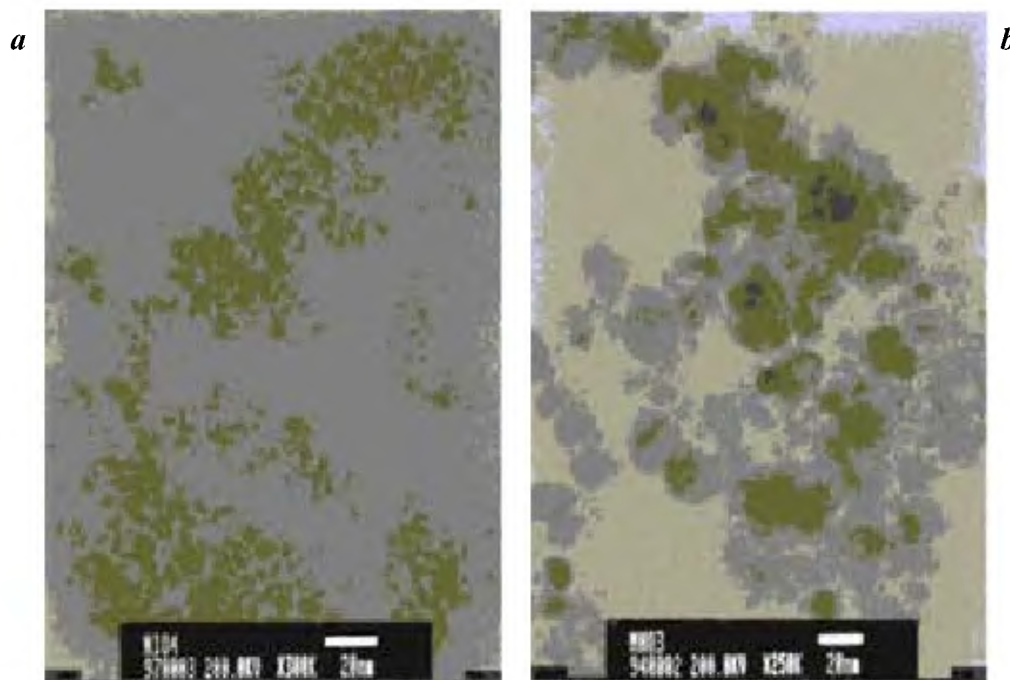
Figure 5. Crystallization under microwave-hydrothermal conditions of nanophase ferrites at about 164°C (100 psi)/4 min: *a*, Ni ferrite and *b*, Mn ferrite.

Figure 6. Crystallization under microwave-hydrothermal conditions of nanophase Ba titanate at 160°C/5 h from Ba and Ti chlorides in the presence of 8 M KOH.
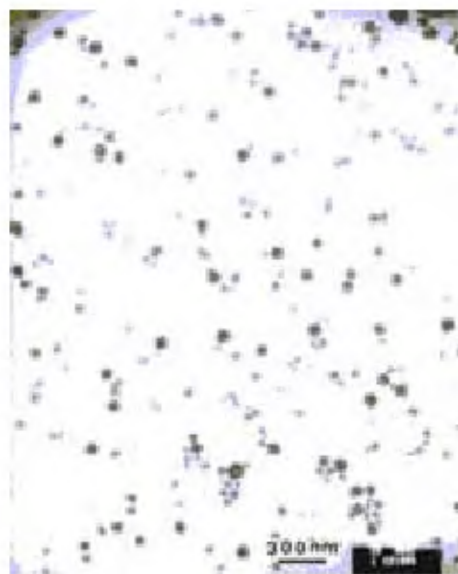
Figure 7. Crystallization of nanophase Pt under microwave-solvo-thermal conditions at 10 psi/15 min.

Microwave-solvothermal or microwave-polyol process for nanophase metals

Nanophase metals such as Pt, Pd, Ag, Au, etc. can be synthesized very rapidly using either ethylene glycol or methanol as reducing agents under microwave-assisted conditions. Figure 7 shows nanophase Pt synthesized in methanol at a pressure of 10 psi in 15 min using H_2PtCl_6 and polyvinylpyrrolidone (PVP) as a capping agent. These nanometal particles have a non-uniform size distribution (Figure 7). The mechanism of reduction by methanol has already been reported in the literature[35]. The methanol reduction process in the microwave field can be described as a microwave-solvothermal process.
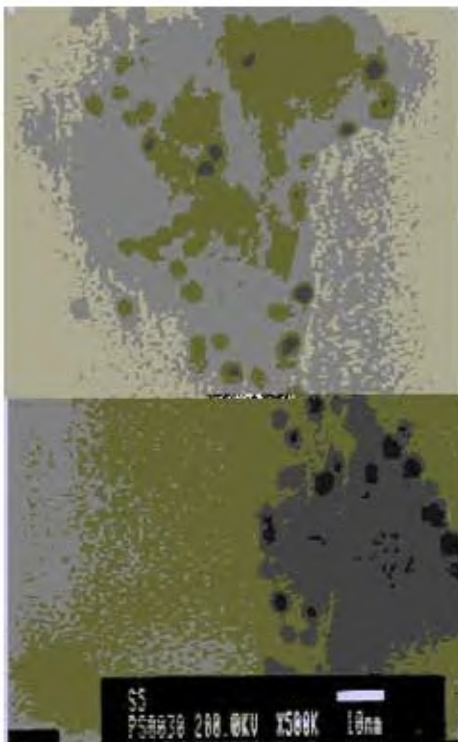
Figure 8. Crystallization of nanophase Pt under microwave-solvo-thermal or microwave-polyol conditions at 200°C/15 min.

Figure 8 shows Pt nanoparticles synthesized at 200°C using H_2PtCl_6 and ethylene glycol in 15 min. A PVP with a molecular weight of 1.3 million was used as a capping agent. The Pt metal nanophases are well dispersed and are about 5 nm in size. Many other metals can be produced using ethylene glycol as a reducing agent and the mechanism of reduction has already been reported in the literature[36]. This process using ethylene glycol (polyol) can be designated as either microwave-solvothermal or more specifically, microwave-polyol process.

Conclusions

Hydrothermal and solvothermal methods are ideally suited for nanophase metal oxide or metal syntheses. The use of microwave field during hydrothermal and solvothermal conditions dramatically enhances their crystallization rate.

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