# Hydrothermal Synthesis of Metal Oxide Fine Particles at Supercritical Conditions

## Tadafumi Adschiri, Yukiya Hakuta, and Kunio Arai\*

Department of Chemical Engineering, Tohoku University, Aoba Aramaki, 980-8579 Sendai, Japan

Supercritical water can provide an excellent reaction environment for hydrothermal crystallization of metal oxide particles. Because of the drastic change of properties of water around the critical point, density, dielectric constant, and ionic product, the phase behavior for the supercritical water—light gas ( $O_2$ ,  $H_2$ , etc.) system and reaction equilibrium/rate can be varied to synthesize new materials or define particle morphologies. In this work, hydrothermal crystallization experiments were performed with several types of flow apparatuses that allow convenient manipulation of variables such as temperature, pressure, and residence time. The proposed supercritical hydrothermal synthesis method has the following desirable features: (1) ultrafine particles can be produced, (2) morphology of the produced particles can be controlled with small changes in pressure or temperature, and (3) a reducing or oxidizing atmosphere can be applied by introducing oxygen, hydrogen, or other gases. An overview of this method is given for functional material synthesis of significant industrial interest including barium hexaferrite magnetic particles, YAG/Tb phosphor fine particles, and lithium cobalt fine crystals.

### Introduction

Hydrothermal crystallization, metal oxide formation from metal salt aqueous solutions, is typically used at temperatures ranging from 373 to 474 K. We are developing hydrothermal crystallization processes that use supercritical water.<sup>1–8</sup> In this work, we refer to this process as supercritical hydrothermal synthesis. The supercritical state of water allows one to vary the reaction rate and reaction equilibrium by shifting the dielectric constant and solvent density with pressure and temperature. Thus, supercritical water can be expected to provide many benefits such as high reaction rates and small particle sizes. From several of our fundamental studies on material production in supercritical water, we have identified the following key features of the supercritical hydrothermal synthesis method: (i) ultrafine particles are produced, (ii) morphology of the produced particles can be controlled to some extent with pressure and/or temperature, and (iii) homogeneous reducing or oxidizing atmospheres can be provided by introducing gases or additional components (O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>).<sup>1</sup> For understanding the mechanism of hydrothermal synthesis at supercritical conditions, our group has conducted solubility measurement<sup>9</sup> and development of estimation methods for metal oxide solubility in high-temperature water.<sup>10</sup> Information has been used in considering the heating requirements necessary in the continuous production of highly functional materials including barium hexaferrite BaFe<sub>12</sub>O<sub>19</sub> magnetic particles,<sup>6</sup> YAG/Tb phosphor fine particles,<sup>7</sup> and Li ion battery cathode material, LiCoO<sub>2</sub>.<sup>8</sup>

The objective of this paper is to clarify the specific features of the supercritical hydrothermal synthesis method by analyzing the previously obtained results in view of kinetic and equilibrium theories. First, the

Table 1.	Lead	Oxide	and	Copper	Oxide	Dissolution
Reaction	l I					

$PbO(s) + 2H^+ \Leftrightarrow Pb^{2+} + H_2O$
$PbO(s) + H^+ \leftrightarrow PbOH^+$
$PbO(s) + H_2O \Leftrightarrow Pb(OH)_2$
$PbO(s) + 2H_2O \Leftrightarrow Pb(OH)_3^- + H^+$
$CuO(s) + 2H^+ \Leftrightarrow Cu^{2+} + H_2O$
$CuO(s) + H^+ \leftrightarrow CuOH^+$
$CuO(s) + H_2O \Leftrightarrow Cu(OH)_2$
$CuO(s) + 2H_2O \Leftrightarrow Cu(OH)_3^- + H^+$

solubility of metal oxides in supercritical water is shown and interpreted with a simple mathematical model. Then, some specific features of supercritical hydrothermal synthesis will be described by showing some experimental results, which are interpreted based on the understanding of the metal oxide solubility and the distribution of chemical species under those conditions. Applications of the hydrothermal crystallization method to be discussed are the continuous production of BaFe<sub>12</sub>O<sub>19</sub>,<sup>6</sup> YAG/Tb,<sup>7</sup> and LiCoO<sub>2</sub><sup>8</sup> particles.

# Solubility of Oxide Species in High-Temperature Water

To study hydrothermal crystallization, information on the solubility of the crystalline substances formed and identification of the ionic species are essential. As examples, the equilibrium reactions for copper and lead oxide are shown in Table 1. For the estimation of the solubility of metal oxides in high-temperature water, the equilibrium constant K for each reaction should be known. The data for equilibrium constants or Gibbs free energy changes for various reactions are available at ambient conditions. The ion product of water,  $K_w$ , is available over a wide range of temperatures and pressures including the supercritical region. Using these data, we proposed a simple correlation model that is applicable even to the supercritical region.<sup>9,10</sup> The following equation includes the Born

<sup>\*</sup> To whom correspondence should be addressed. E-mail: karai@arai.che.tohoku.ac.jp. Fax: +81-22-217-7246.



**Figure 1.** Dielectric factor for water plotted against 1/*T*.



**Figure 2.** Solubility behavior of CuO in sub- and supercritical water: (**•**) 280 bar; Sue et al.,<sup>8</sup> ( $\bigcirc$ ) 280 bar; ( $\triangle$ ) saturation pressure; Hearn et al.<sup>9</sup>

term, which expresses an electrostatic interaction of ion with dielectric field,

$$\ln K(T,\rho) = \ln K(T_0,\rho_0) + \left(\frac{\partial \ln K}{\partial(1/T)}\right)_{\rho_0} \left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{\omega}{T} \left(\frac{1}{\epsilon(T,\rho)} - \frac{1}{\epsilon_0(T_0,\rho_0)}\right)$$
(1)

where *K* is an equilibrium constant, *T* is the absolute temperature,  $\epsilon$  is a dielectric constant, and  $\omega$  is a parameter determined by a reaction system.

Figure 1 shows the dielectric factor as a function of temperature and pressure. Water at ambient temperature and pressure was chosen as the reference state. At the reference density and over a wide range of temperatures, the dielectric factor is small enough to be considered negligible. On the other hand, at the lower pressures, the dielectric factor becomes large especially above the critical temperature.

The solubility of copper oxide is shown in Figure 2.9-11 Curves shown in this figure are the solubilities estimated by the model, with the term  $\omega$  being treated as a fitting parameter for each dissociation reaction. Evaluation of  $\omega$  by using the database of the Helgeson– Kirkham-Flowers model<sup>12</sup> is also available. As shown here, the measurements could be correlated adequately especially in the retrograde region around the critical point. The solubility of metal oxide varies with the existing cation and anion and the pH of the solution. In general, the solubility decreases, showing the minimum, and then increases with elevating pH at constant temperature. The pH showing the minimum solubility shifts toward lower pH with increasing temperature, because of the increase of the  $K_w$  for water. One more important point is the distribution of the ionic species in solution. As shown in Figure 2, the Cu<sup>2+</sup> species does not exist at conditions above about 200 °C. From 300 to 400 °C the single charge cation and anion copper species sharply decrease and neutral solute increases and dominates the solubility behavior above 400 °C at 280 bar. As discussed later, understanding the temperature



Figure 3. Experimental apparatus.

and pH dependence of the solubility and of the distribution of chemical species is the key to providing the optimum condition for supercritical hydrothermal synthesis.

# **Specific Features of Hydrothermal Synthesis under Supercritical Conditions**

**Experimental Section.** Figure 3 shows a typical experimental apparatus that we use for hydrothermal crystallization syntheses. An aqueous metal salt solution is prepared and fed into the apparatus in one stream. In another stream, distilled water is pressurized and then heated to a temperature that is above the temperature desired. The pressurized metal salt solution stream and the pure supercritical water stream are then combined in a mixing point. This leads to rapid heating and subsequent reaction in the reactor. After the solution leaves the reactor, it is rapidly quenched and in-line filters remove larger particles. Pressure is controlled with a backpressure regulator. The fine particles are collected in the effluent. Productivity of the metal oxide particles is determined by the feed rate of the feed solution (3-5 mL/min) and its concentration (0.001-0.1 mol/L). Thus, the production rate of the metal oxide in this experiment was in the range from 0.1 to 10 g/h.

**Specific Features.** In this section, the specific features of the supercritical water crystallization were summarized. Table 2 shows products obtained in the previous experiments with a flow-type apparatus.<sup>1-8</sup> Metals used were Fe, Al, Ni, Co, Ti, and Zr and the anions were  $NO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^-$ , and ammonium citrate. As shown here, this method could be applied for various systems to produce metal oxide fine particles.

(a) Ultrafine Particles Formation. Figure  $4^1$  shows typical scanning electron microscopy (SEM) photos for the obtained particles (TiO<sub>2</sub> and ZrO). The particle size obtained under these conditions was 20-50 nm. As shown in this figure and in Table 2, with the supercritical hydrothermal crystallization method, particle sizes in the range from 10 to 1000 nm can be produced. In many cases, particles have well-developed crystal faces, which suggests single crystals.

The particle size seems to be most strongly influenced by the initial concentration of the feed and heating rate, and thus ultrafine particles can be formed even at subcritical conditions.<sup>13–15</sup> Here, we compare the size of the particles obtained at subcritical and supercritical

 Table 2. Metal Oxide Particles Produced by the

 Supercritical Hydrothermal Synthesis Technique

metal salt used as the starting material	product	particle size [nm]	morphology	ref
Al(NO <sub>3</sub> ) <sub>3</sub>	Alooh	80-1000	hexagonal plate rhombic needlelike	1, 2, 7
Fe(NO <sub>3</sub> ) <sub>2</sub>	α-Fe <sub>2</sub> O <sub>2</sub>	$\sim 50$	spherical	1
$Fe_2(SO_4)_3$	α-Fe <sub>2</sub> O <sub>3</sub>	$\sim 50$	spherical	1
FeCl <sub>2</sub>	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	${\sim}50$	spherical	1
$Fe(NH_4)_2H(C_6H_5O_7)_2$	Fe <sub>3</sub> O <sub>4</sub>	${\sim}50$	spherical	1
$Co(NO_3)_2$	Co <sub>3</sub> O <sub>4</sub>	$\sim \! 100$	octahedral	1
Ni(NO <sub>3</sub> ) <sub>2</sub>	NiO	$\sim 200$	octahedral	1
ZrOCl <sub>2</sub>	ZrO <sub>2</sub> (cubic)	$\sim \! 10$	spherical	1
Ti(SO <sub>4</sub> ) <sub>2</sub>	TiO <sub>2</sub>	$\sim 20$	spherical	1
TiCl <sub>4</sub>	TiO <sub>2</sub> (anatase)	$\sim 20$	spherical	1
Ce(NO <sub>3</sub> ) <sub>3</sub>	CeO <sub>2</sub>	20 - 300	octahedral	3, 4
$Fe(NO_3)_3$ , $Ba(NO_3)_2$	BaO•6Fe <sub>2</sub> O <sub>3</sub>	50-1000	hexagonal plate	6
Al(NO <sub>3</sub> ) <sub>3</sub> , Y(NO <sub>3</sub> ) <sub>3</sub> , TbCl <sub>3</sub>	Al <sub>5</sub> (Y+Tb) <sub>3</sub> O <sub>12</sub>	20-600	dodecahedral	7
Li(NO <sub>3</sub> ), Co(NO <sub>3</sub> ) <sub>2</sub>	LiCoO <sub>2</sub>	40 - 400	dodecahedral	8

conditions by using the same apparatus and keeping the feed concentration and feed rate the same.

Figure 5a shows ceria fine particles obtained at 573 K and 30 MPa from Ce(NO<sub>3</sub>)<sub>3</sub>. The SEM photographs show the reaction at increasing residence time. Using reactors of different lengths varied the residence times. Cloudlike products with fine crystals were observed at 0.7 s. These cloudlike products tended to disappear, and crystal particle sizes increased with reaction time. Figure 5b shows the particle formation in supercritical water at 673 K and 30 MPa. For this case, no cloudlike products were observed even at very short residence times. Further, as shown in the photograph, there was little change in the particle size with residence time, indicating that the reaction was complete. The particle size was approximately 18 nm.

Supercritical water hydrothermal synthesis reactions proceed faster than the corresponding reactions in subcritical water. One reason for this is because the lower dielectric constant results in an enhancement of the reaction rate, *k*, according to the theory of Born:

$$\ln k = \ln k_0 - \frac{\omega}{RT} \left( \frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right)$$
(2)

where  $\omega$  is a constant determined by a reaction system,  $\epsilon$  is the dielectric constant,  $k_0$  is the reaction rate at dielectric constant  $\epsilon_0$ , R is the gas constant, and T is the absolute temperature.

We examined the reaction rate above the critical point in a series of experiments using different lengths of reactors; namely, a different reaction time, *t*, was conducted for the Al(NO<sub>3</sub>)<sub>3</sub> system. From the decrease of the concentration of the Al ion in the effluent, the conversion degree of the Al ion, *X*, was determined. The apparent first-order reaction rate constant, *k*, was evaluated from the slope of the plot of  $-\ln(1 - X)$  versus *t*, as shown in Figure 6. Figure 7 is the Arrhenius plot of the first-order rate constant evaluated. In the range of subcritical temperature, the rate constant fell on a straight line, but above the critical temperature, the reaction rate seemed to greatly increase, as shown by the data in Figure 7. This enhancement in rate in the critical region is also predicted by eq 2.

After fast nucleation, crystal growth occurs through further addition of intermediates. In subcritical water, the solubility of intermediate species is expected to be high. The cloudlike products observed only in subcritical water experiments probably are a result of aggregation of intermediate species. At supercritical conditions, the solvent power of supercritical water is much less than that of subcritical water, and the solubility of intermediates is very low. Therefore, a very high degree of supersaturation exists, and rapid nucleation occurs. Intermediates are consumed at the nucleation stage, and ultrafine particles are obtained.<sup>3,4</sup> A schematic mechanism of CeO<sub>2</sub> formation in sub- and supercritical water is shown in Figure 8.

(b) Control of the Oxidizing or Reducing Atmosphere with O2 or H2. When ferrous ammonium citrate is used as the feed, magnetite (Fe<sub>3</sub>O<sub>4</sub>) particles are formed<sup>1</sup> in a single phase. For this case, Fe(III) is reduced to Fe(II), which is probably due to the reduction of Fe(III) by CO formed by the thermal decomposition of ammonium citrate. Because CO is miscible with supercritical water, a homogeneous reaction atmosphere is provided, which allows for magnetite particles to form in a single phase. Formation of a homogeneous phase for supercritical solution and light gases provides a uniform oxidizing or reducing environment, and this probably promotes the oxidizing/reducing capability, when  $O_2$  or  $H_2$  gas is introduced. This is discussed later for the oxidative production of  $LiCoO_2$  from  $Co(NO_3)_2$ and LiOH, which considers the introduction of oxygen gas.

(c) Control of Morphology. When aluminum nitrate was used as the starting material, particles of a variety of morphologies were obtained around the critical point. An aluminum nitrate aqueous solution was heated rapidly to reaction temperatures by mixing with supercritical water at a mixing point. As shown in Figure 9, various morphologies could be found.<sup>2</sup>

In previous literatures, <sup>16–18</sup> it was demonstrated that morphology changes with the feed concentration, pH, and type of salt in subcritical hydrothermal conditions. The results in Figure 9 show that the morphology changed with temperature and pressure especially around the critical point.<sup>2</sup> This is most likely due to the change of properties of water, especially the dielectric constant and ion product of water. We have studied the relation between the crystal habit of boehmite (AlOOH) particles and the chemical equilibrium in hydrothermal conditions. The results are schematically shown in Figure 10. Calculation results of the aluminum ion species distribution in the crystallization atmosphere suggest that AlOOH particle morphology is determined by selective adsorption of positively charged species, Al- $(OH)^{2+}$  or Al $(OH)_{2+}$ , on the negatively charged surface of the AlOOH crystal.<sup>5</sup> Around the critical point, the equilibrium constant of the chemical reaction changes greatly with the temperature and pressure. This leads to a change in the chemical species distribution and thus the crystal habits.

### Applications of the Method for Producing Complex Metal Oxides

**Formation of Barium Hexaferrite and YAG/Tb Phosphor.** The supercritical hydrothermal crystallization method was applied to the production of complex metal oxides, (i) barium hexaferrite  $(BaFe_{12}O_{19})^6$  used in high-density recording media, (ii) metal-doped oxide  $(Al_5(Y+Tb)_3O_{12}, YAG/Tb)^7$  used in phosphor screens, and (iii) lithium cobalt oxide (LiCoO<sub>2</sub>) used in Li ion battery cathodes. The experimental apparatus for the produc-



Figure 4. (a)  $ZrO_2$  particles obtained from 0 to 2 M  $ZrCl_2O$  at 673–763 K and 30 MPa. (b)  $TiO_2$  (anatase) particles obtained from 0.01 M  $TiCl_4$  at 673 K and 30 MPa.



Figure 5. (a) CeO<sub>2</sub> obtained at 573 K and 30 MPa. (b) CeO<sub>2</sub> obtained at 673 K and 30 MPa.



**Figure 6.**  $-\ln(1 - X)$  vs time curves (Al(NO<sub>3</sub>)<sub>3</sub>). Concentration: 0.01 mol/L. Pressure: 30 MPa.

tion of barium hexaferrite is shown in Figure 11. A mixture of  $Ba(NO_3)_2$  and  $Fe(NO_3)_3$  was mixed with a KOH solution, and after preheating the solution, the mixture was combined with supercritical water at a mixing point. The preheating was found to be essential for good results. The solubility estimation by eq 1 suggests that the solubility of  $Fe(OH)_3$  or  $Ba(OH)_2$  increases with temperature in the higher pH region. Thus, mixing with supercritical water at the second mixing point could be achieved in a homogeneous phase. By this method, barium hexaferrite particles could be continuously produced with a large excess of  $Ba(NO_3)_2$ 

Figure 7. Arrhenius plot of the apparent first-order rate constant.

against Fe(NO<sub>3</sub>)<sub>3</sub> and at OH/NO<sub>3</sub> higher than 4. The reaction time required was approximately 1 min. The commercial method is a batchwise high-temperature solid-state method. The products of BaO·6Fe<sub>2</sub>O<sub>3</sub> obtained in this experiment were 100 nm size hexagonal plate shaped particles, while a commercially produced product has a more rounded appearance and is larger, being on the order of 1  $\mu$ m in size. Magnetic properties of the produced particles (Coercivity 1724 Oe and saturation magnetization 51.2 emu/g) were comparable with those of commercial products (Coercivity 880 emu/g and saturation magnetization 54 emu/g; Toshiba). The supercritical technique does not require heat treatment.



Figure 8. Schematic of CeO<sub>2</sub> formation.

For producing barium hexaferrite in a short reaction time, one important point is the barium ion ratios. Figure 12 shows X-ray diffraction patterns for various reaction products produced under supercritical conditions. The diffraction pattern for the barium ion stoichiometric ratio of 1:12, only  $\alpha$ -hematite was precipitated. As described above for the experimental method, preheating of the BaOH-Fe(OH)<sub>3</sub> gel (523 K and 0.5 min) before the supercritical crystallization is essential for producing barium hexaferrite in a single phase. As the ratio of barium to iron is elevated, barium hexaferrite starts to form along with the hematite. For the higher barium iron ratios, only barium hexaferrite precipitates as a single solid phase for 1 min of reaction time. For these cases, further heating of the mixture caused the conversion of some barium hexaferrite to barium diferrite. That is, diferrite is the equilibrium product under these conditions. So, most remarkably, this means that at these ratios the metastable product is produced under supercritical conditions.

We also conducted a series of experiment in a subcritical temperature at 523 K using the same apparatus and with the same feed concentration and feed rate. Also at this temperature, production of BaO·6Fe<sub>2</sub>O<sub>3</sub> in a single phase was achieved. The particle size was around 1  $\mu$ m, and particles were thinner than the particles obtained by the supercritical hydrothermal synthesis method. However, the magnetic properties obtained (Coercivity 1622 Oe and saturation magnetization 35.1 emu/g) were less favorable than those of the latter method. Thermogravimetric analysis of the particles obtained in a nitrogen atmosphere showed a 3 wt % decrease of the weight in 473-673 K, while that for the particles obtained by the supercritical synthesis method shows little decrease of the weight. This suggests the desorption of water or OH groups, and this might be the reason for the difference in magnetic properties at subcritical conditions.

Another example is for YAG/Tb phosphor synthesis.<sup>7</sup> The commercial method for the YAG phosphor synthesis is via a batchwise solid-state reaction at 2300 K. During the process, two phases form (AlYO<sub>3</sub> and Al<sub>2</sub>Y<sub>4</sub>O<sub>7</sub>). Long reaction times are required to transform the two-phase system into a single-phase YAG. The doping of Tb (an activator ion) onto the  $Y_3Al_5O_{12}$  (YAG) crystal is made after producing it. In the proposed process, a mixed solution of Y(NO<sub>3</sub>)<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, and TbCl<sub>3</sub> were used. It was demonstrated that single-phase YAG/Tb particles could be produced at 673 K and 30 MPa in 1 min. The luminescence properties of obtained YAG/Tb particles were comparable with that of particles produced by the

conventional solid-state reaction at high temperature, which requires long reaction times.

LiCoO<sub>2</sub> Production. Applications for producing LiCoO<sub>2</sub> double oxides are expected to be of importance because of commercial applications in battery technologies. For a good electrochemical performance, smaller particle size with high crystallinity is required for LiCoO<sub>2</sub>. However, it is difficult to reduce the particle size to a submicron order by conventional solid-state reactions followed by comminution steps. For liquidphase synthesis methods, where a  $Co^{2+}$  ion is the starting species, the oxidation conditions for Co<sup>2+</sup> do not always match that required for the crystallization atmosphere. By using the supercritical hydrothermal synthesis method, we thought ultrafine particles could be produced and the effective oxidation of  $Co^{2+}$  with  $O_2$ could take place because a homogeneous reaction atmosphere would be formed between  $O_2$  and aqueous solutions under supercritical conditions.

The above specific features of the supercritical hydrothermal crystallization method are attractive for producing fine LiCoO<sub>2</sub> crystals. Experiments were performed with a similar type of apparatus shown in Figure 11. A Co(NO<sub>3</sub>)<sub>2</sub> aqueous solution (0.02 M) was first mixed with a LiOH aqueous solution (0.4 M) at a mixing point. For oxidizing a Co<sup>2+</sup> ion in the reaction atmosphere, O<sub>2</sub> gas was introduced into the reactor after decomposing a H<sub>2</sub>O<sub>2</sub> aqueous solution (0.07 M). The mixed solution of LiOH and Co(NO<sub>3</sub>)<sub>2</sub> was contacted with a supercritical water–oxygen mixture fed from another line. At the supercritical water mixing point, solutions were rapidly heated to the reaction temperature (573, 623, or 673 K) and hydrothermal crystallization occurred.

Figure 13 shows X-ray diffraction (XRD) patterns for the particles produced. This figure clearly indicates that LiCoO<sub>2</sub> particles were produced in a single phase at 673 K and 30 MPa. The LiCoO<sub>2</sub> particles were found to have rock salt type structure belonging to the *Fd*3*m* space group. However, at 573or 623 K, Co<sub>3</sub>O<sub>4</sub>, which is composed of Co<sup>2+</sup> and Co<sup>3+</sup>, was produced. Thus, at supercritical conditions, a more effective oxidation of Co<sup>2+</sup> took place than at 573or 623 K. One reason for this is because of the homogeneous oxidizing atmosphere and reaction environment. Figure 14 shows transmission electron microscopy (TEM) and electron diffraction images of lithium cobalt oxide synthesized in supercritical water with our method.8 The dodecahedron particles had well-developed crystal faces, and the electron diffraction pattern provided conclusive evidence that the particles were single crystals. It should be pointed out that single-crystal particles have vet to be synthesized by the commercial solid-state reaction method.

The electrochemical characterization was performed by a constant current discharge and charge, where a mixed solvent of ethylene carbonate and diethyl carbonate containing 1.0 M LiClO<sub>4</sub> was used as the electrolyte. At the first charge, the capacity was 153 mA h g<sup>-1</sup>, which was larger than 150 mA h g<sup>-1</sup> of the theoretical capacity. The discharge capacity slightly decreased with discharge and charge cycles. However, the discharge ratio decreased after a given number of cycles, which was around half of that for materials obtained by the conventional solid-state method. This small decrease in the discharge capacity indicates a high reversibility of



**Figure 9.** AlOOH fine particles obtained at various reaction conditions: (a) 0.02 M Al(NO<sub>3</sub>)<sub>3</sub>, 650 K, 35 MPa; (b) 0.05 mol/L, 373–573 K, 30 MPa; (c) 0.006 mol/L, 623 K, 35 MPa; (d) 0.05 mol/L, 673 K, 40 MPa.



**Figure 10.** Variation of the morphology of AlOOH around the critical point.



Figure 11. Experimental apparatus for barium ferrite, YAG/Tb, and LiCoO<sub>2</sub>.



Figure 12. XRD profiles of BaO·6Fe\_2O\_3 particles obtained: (O) BaO·6Fe\_2O\_3; ( $\bigtriangledown$ )  $\alpha$ -Fe\_2O\_3.

the lithium insertion and extraction processes, which means that  $LiCoO_2$  prepared by our method has a very high stability. These favorable characteristics are probably due to the single crystalline nature of the produced particles.





TEM Electron Diffraction Figure 14. TEM photograph of LiCoO<sub>2</sub> fine particles and their electron diffraction pattern.

#### Conclusions

The specific features of the supercritical hydrothermal synthesis method are (i) quantitative production of ultrafine particles and (ii) control of the particle morphology or the crystal structure by varying the pressure, temperature, or reaction atmosphere (reducing or oxidizing).

The supercritical hydrothermal synthesis method was applied for the production of barium hexaferrite, YAG/ Tb phosphor, and a lithium ion battery material, LiCoO<sub>2</sub>. By rapid heating of the reactant solutions, continuous production of the metal oxide fine particles could be achieved. An understanding of the metal oxide and ionic species solubility is essential for determining process conditions. For the production of LiCoO<sub>2</sub>, oxygen In conclusion, the general features of the supercritical hydrothermal synthesis method can be expected to open the door to a wide range of new applications in material production. Material production with the supercritical hydrothermal synthesis method can be expected to have a bright future.

### Acknowledgment

The authors acknowledge the Ministry of Education, Science, Sports and Culture, Japan, Genesis Research Institute, and New Energy and Industrial Technology Organization (NEDO) for financial support of this research.

#### **Literature Cited**

(1) Adschiri, T.; Kanazawa, K.; Arai, K. Rapid and Continuous Hydrothermal Crystallization of Metal Oxide Particles in Supercritical Water. *J. Am. Ceram. Soc.* **1992**, *75*, 1019–1023.

(2) Adschiri, T.; Kanazawa, K.; Arai, K. Rapid and Continuous Hydrothermal Synthesis of Boehmite Particles in Subcritical and Supercritical Water. J. Am. Ceram. Soc. **1992**, *75*, 2615–2620.

(3) Hakuta, Y.; Terayama, H.; Onai, S.; Adschiri, T.; Arai, K. Production of Ultra Fine Ceria Particles by Hydrothermal Synthesis under Supercritical Conditions. *J. Mater. Sci. Lett.* **1998**, *17*, 1211–1213.

(4) Hakuta, Y.; Onai, S.; Adschiri, T.; Arai, K. Hydrothermal Synthesis of CeO<sub>2</sub> Ultra Fine Particle in Supercritical Water. *Proc. Int. Symp. Supercrit. Fluids B* **1997**, 255–259.

(5) Hakuta, Y.; Adschiri, T.; Hirakoso, H.; Arai, K. Chemical Equilibria and Particle Morphology of Boehmite (AlOOH) in Sub and Supercritical Water. *Fluid Phase Equilib.* **1999**, *158–160*, 733–739.

(6) Hakuta, Y.; Adschiri, T.; Suzuki, T.; Seino, K.; Arai, K. Flow Method for Rapidly Producing Single Phase Barium Hexa-ferrite Particles in Supercritical Water. *J. Am. Ceram. Soc.* **1998**, *81* (9), 2461–2465. (7) Hakuta, Y.; Seino, K.; Ura, H.; Adschiri, T.; Takizawa, H.; Arai, K. Production of phosphor (YAG/Tb) fine particles by hydrothermal synthesis in supercritical water. *J. Mater. Chem.* **1999**, *9* (10), 2671–2675.

(8) Adschiri, T.; Hakuta, Y.; Kanamura, K.; Arai, K. Continuous Production of LiCoO<sub>2</sub> Fine Crystals for Lithium Batteries by Hydrothermal Synthesis under Supercritical Condition. *J. High-Pressure Sci.* 2000, in press.

(9) Sue, K.; Hakuta, Y.; Smith, R. L., Jr.; Adschiri, T.; Arai, K. Solubility of Lead(II) Oxide and Copper(II) Oxide in Subcritical and Supercritical Water. *J. Chem. Eng. Data* **1999**, *44*, 1422–1426.

(10) Sue, K.; Hakuta, Y.; Smith, R. L., Jr.; Adschiri, T.; Arai, K. Measurement and Correlation of Metal Oxides Solubility in suband supercritical water. *13th Int. Conf. Prop. Water Steam* **1999**, *1*, 145–145.

(11) Hearn, B.; Hunt, M.; Hayward, A. Solubility of Cupric Oxide in Pure Subcritical and Supercritical Water. *J. Chem. Eng. Data* **1969**, *14*, 442–447.

(12) Tanger, J. C.; Helgeson, H. C. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Temperatures: Revised Equations of State for the Standard Partial Molal Properties of Ions and Electrytes. *Am. J. Sci.* **1988**, *288*, 19–98.

(13) Matijevic, E.; Hsu, W. P. Preparation and Properties Monodispersed Colloidal Particles of Lanthanide Compounds. 1. Gadolinium, Europium, Terbium, Samarium, and Cerium(III). *J. Colloid Interface Sci.* **1987**, *118* (2), 506–523.

(14) Hirano, M.; Kato, E. The Hydrothermal Synthesis of Ultrafine cerium(IV) oxide powders. *J. Mater. Sci. Lett.* **1996**, *15*, 1249–1251.

(15) Dawson, W. J. Hydrothermal Synthesis of Advanced Ceramic Powders. Am. Ceram. Soc. Bull. **1988**, 67, 1673–1678.

(16) Scott, W. B.; Matijevic, E. Preparation of uniform Particles by hydrolysis of Aluminum Chloride and Perchlorate Salts. *J. Colloid Interface Sci.* **1978**, *66* (3), 447–454.

(17) Brown, N. Hydrothermal Crystallization of  $\alpha$ -alumina monohydrate in the presence of copper ions. *J. Cryst. Growth* **1989**, *97*, 387–392.

(18) Buining, P. A.; Pathmamanoharan, C.; Bosboom, M.; Jansen, J. B. H.; Lekkerkerker, H. N. W. Effect of Hydrothermal Conditions on the Morphology of Colloidal Boehmite Particles: Implication for Fibril Formation and Monodispersity. *J. Am. Ceram. Soc.* **1990**, *73* (8), 2185–2390.

Received for review March 17, 2000 Revised manuscript received October 17, 2000 Accepted October 19, 2000

IE0003279