CHAPTER II

THEORITICAL BACKGROUND AND LITERATURE REVIEW

2.1 Physical and Chemical Properties of Bismuth

Bismuth, the 83rd element of the periodic table, is the most metallic and the least abundant of the element in nitrogen family (group 15). It also exhibits many properties similar to those of semiconductors and insulators. Bismuth is a soft, heavy, lustrous, silver-white metal with a slight pink tinge. It forms large brittle crystals with a highly intricate feature of step dislocation when the melt is left to cool slowly. Under high pressure, bismuth undergoes several allotropic transformations, involving change in volume. Bismuth is one of the two metals that expand slightly on solidification, 3.32%.

Bismuth is the heaviest member of group 15 and the heaviest stable element on the periodic table. Although it belongs to the group 15 family, the chemistry of bismuth differs considerably from that of other lighter members. Decreasing availability and increasing diffuseness of *s* electrons makes the +5 oxidation state less stable when comparing with phosphorus, arsenic and antimony.

Bismuth is inert in dry air at room temperature, but oxidized slowly to become a thin film of the oxide. It is oxidized rapidly to form an oxide film above the melting point, and burnt with a bluish flame to give a yellow fume of bismuth oxide (Bi_2O_3) at red heat in air. It also can be attacked by super-heated water vapor to form yellow oxide.

Bismuth is generally dissolved in nitric acid to give bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$) with the evolution of nitrogen oxide, and in hot sulfuric acid to give sulfur dioxide, forming bismuth sulphate ($Bi_2(SO_4)$). Further heating of bismuth with concentrated hydrochloric acid gives bismuth chloride ($BiCl_3$), which is sublimed in air, and partly converted to bismuth oxychloride ($BiOCl$).

2.2 Bismuth Alkoxide

Bismuth alkoxide can be synthesized by many methods. There are metathesis (A), alcohol-amine exchange (B), alcohol-alcohol exchange (C), benzene elimination (D), electrochemical oxidation (E), and alcoholysis (F), as shown in Figure 1.

$$\mathrm{BiCl_3 + 3MOR \longrightarrow [Bi(OR)_3]} \qquad \textbf{(A)}$$

$\mathrm{M = Li, Na, K}$

$$\mathrm{[Bi(NR'_2)_3] + 3ROH \longrightarrow [Bi(OR)_3]} \qquad \textbf{(B)}$$

$\mathrm{R' = Me, SiMe_3}$

$$\mathrm{[Bi(OR'_3) + 3ROH \longrightarrow [Bi(OR)_3]} \qquad \textbf{(C)}$$

$$\mathrm{BiPh_3 + 3ROH \longrightarrow [Bi(OR)_3]} \qquad \textbf{(D)}$$

$$\mathrm{Bi + 3ROH \longrightarrow [Bi(OR)_3]} \qquad \textbf{(E)}$$

$$\mathrm{Bi(OH)_3 + 3ROH \longrightarrow [Bi(OR)_3]} \qquad \textbf{(F)}$$

Figure 2.1 Methods used to synthesize bismuth alkoxide.

Aminoalcohols represent another class of alcohols used to a large extent in sol-gel processing. Mono- and di-ethanolamines were found to give access to media remaining homogeneous even for large hydrolysis ratios h ($h = [\mathrm{H_2O}]/[\mathrm{M(OR)_n}]$), up to 10, for instance, $\mathrm{M(OR)_4}$-deaH$_2$-H$_2$O-iPrOH (M = Ti, Zr) (Takahashi, 1988). Various ethanolamines have been used as sol stabilizers (Ohya, 1992) and/or as a means to improve the microstructure of coatings (Tanaka, 1995). Primary and secondary aminoalkoxides of $\mathrm{OHCHRCH_2NMe_2}$ type have been proven to be more efficient than 2-methoxyethoxide for breaking down aggregation and, thus, providing volatility. However, most reported mixed ligand alkoxides were derived from the modification of metal alkoxides. The essential feature of metal alkoxides is the liability of the M–OR bond (Chisholm, 1992; Hubert-Pfalzgraf, 1992). This property is usually retained for functional alkoxides and modifications can occur easily. The ability of triethanolamine ($\mathrm{N(C_2H_4OH)_3}$, teaH$_3$) to stabilize transition metal alkoxides, such as those of titanium toward hydrolysis, has been known earlier. The extensive possibilities of hydrogen bondings (intra and intermolecular via the non-deprotonated hydroxyls) favor the formation of gels, but are defavorable to a facile elimination of the organic residues if crystalline materials are required. Functional bismuth alkoxides which usually show improved hydrolytic stability remain limited to a few alkoxyalkoxides, such as aminoalkoxides, $Bi(OCHRCH_2NMe_2)_3$ (R= H or Me) (Matchett, 1990), $Bi(tea)_3$ (Bachman, 2003). The triethanoaminolate, $[Bi(OCH_2CH_2)_3N]$ was obtained by reacting freshly prepared $Bi(OH)_3$ in alcohol with $teaH_3$ and sodium, but no yield was reported (Kadokura, 2005).

The glycolate ligand is the one of interest as precursor due to its stability toward moisture. The alcoholysis of $Bi(NO_3)_3.5H_2O$ by polyols afforded heteroleptic derivatives (Rogers, 1992). In 1992, Zewaco *et al.* synthesized bismuth ethylene glycolate by heating bismuth oxide at boiling ethylene glycol, giving 98 % yield as a gray precipitate. Recently, bismuth glycolate was observed during preparation of elemental bismuth by so-called polyol process. Goia *et al.* also obtained bismuth glycolate intermediated via heating bismuth salts, such as $Bi(NO_3)_3.5H_2O$, $Bi(OH)_3$, and $Bi(Cl)_3$ in polyol (Goia, 2005). Li *et al.* obtained the glycolate precursor as intermediate during the preparation of bismuth nanoparticles (Li^d, 2009).

2.3 Polyol Process

Heating metal salts and metal oxide in polyol media, such as propylene glycol, ethylene glycol, or glycerol, is so-called "polyol process". This process was developed by Michel Figlarz, Fernand Fiévet, and Jean-Pierre Lagier at the University of Paris (Figlarz, 1985). Many types of precursors can be widely used, such as hydroxides, oxides, nitrate, acetate and sulfates. Polyol itself can act as solvent and reducing agent, depending on the elementary condition. The reaction mechanism of polyol was widely discussed. Firstly, metal precursor becomes solubilized in diol, forming an intermediate, followed by being reduced to form metal nuclei. Joseyphus *et al.* (Joseyphus, 2007) found that cobalt was prior formed complex alkoxide as cobalt glycolate precursor before being reduced to metal.

Other metals, such as Ti (Wang[a], 1999), Cu (Sun, 2005), Fe (Zhong[a], 2006), are also capable to coordinate and form glycolate complex.

Although a number of metallic (i.e. Cd, Bi, Rh, Ru) preparation in polyol medium has been reported, theoretically the understanding for predicting metal reduction potential was firstly investigated by Lacher and Patric in 2000 (Larcher, 2000). They studied the thermodynamic approach of the preparation of metallic powders and alloys in ethylene glycol media. The overall reduction reaction of the metal oxides in boiling ethylene glycol can be written as

$$CH_2OH\text{-}CH_2OH_{(l)} + 5/xMO_{x(s)} \longrightarrow 5/xM^0_{(s)} + 2CO_{2(g)} + 3H_2O_{(g)} \qquad (1)$$

The Gibb free energies of the formation of $2CO_{2(g)}$, $5/xMO_{x(s)}$, $3H_2O_{(g)}$, and $CH_2OH\text{-}CH_2OH_{(l)}$ were calculated from the studies of Lide (Lide, 1992), Reed (Reed, 1971), James *et al.* (James, 1992), Barin *et al.* (Barin, 1973), Pourbaix (Pourbaix, 1963) and Parks[a,b,c] (Parks, 1929; 1925). The ΔG for M^0 was taken to be zero at any temperature. They found that the formation of either liquid or gaseous water resulted in only small deviation in overall ΔG_{red}, and was calculated as follow;

$$\Delta G_{red} = 2\Delta G_f(CO_2) + 3\Delta G_f(H_2O) - 5/x\Delta G_f(MO_X) - \Delta G_f(EG) \qquad (2)$$

The calculation result is illustrated in Figure 2.2. The vertical bars indicate the ranges of the ΔG_{red} values, taking into account the discrepancies in thermodynamics values listed in the literature for the ΔG_f value. The shadowed labels showed that particular oxide had not been successfully reduced to metal in the boiling point of ethylene glycol. In contrast, all of the oxides experimentally reduced to metal (not shadowed in Figure 2.2) showed a negative ΔG_f. Because this calculation was performed by assuming a total oxidation of ethylene glycol, in practical, this reaction path could be invalid. However, it can be used to predict the reduction potential of particular metal. For instance, the negative free energy values of silver and palladium showed that they can be easily reduced in ethylene glycol. Jiu *et al.* (Jiu, 2009) synthesized Ag nanorods with high yield by this polyol process.

With the assistance of poly(vinyl pyrrolidone), the silver nitrate was completely reduced at 150 °C within 1.5 h.

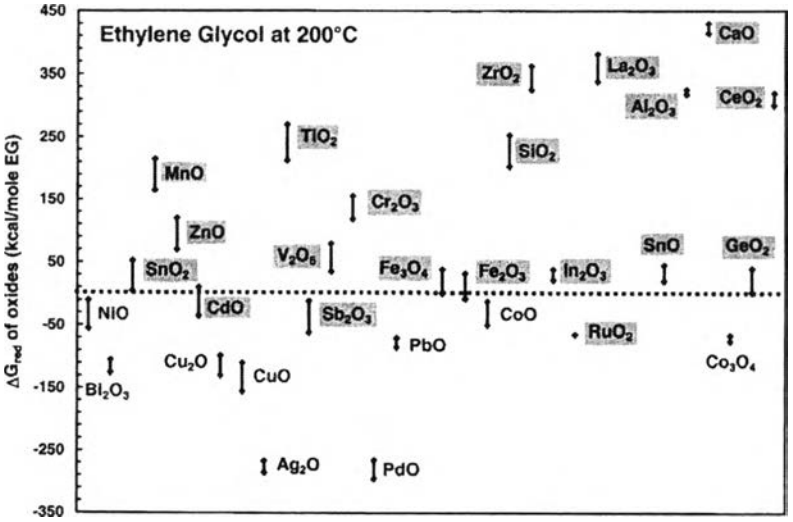


Figure 2.2 Calculated ΔG of reduction (ΔG_{red}) by ethylene glycol at 200 °C for various oxides assuming a total oxidation of the alcohol and the formation of the metal according to reaction in equation (1). The shadowed and nonshadowed labels indicate experimentally nonreduced and reduced oxides, respectively.

However, the reduction reaction was not passed through the metal salts to elemental. The formation of the metal comes with the formation of intermediate reactive phase, such as oxides, or alkoxides. Lacher and Patrice (Larcher, 2000) provided some insights that the formation of metal came from intermediated reactive phase, such as reduced oxides and/or alkoxides, as shown in Figure 2.3, showing that the metal is directly formed or after the precipitation of the alkoxide. Each reaction step can be slowed down or blocked by solubility or kinetic issues.

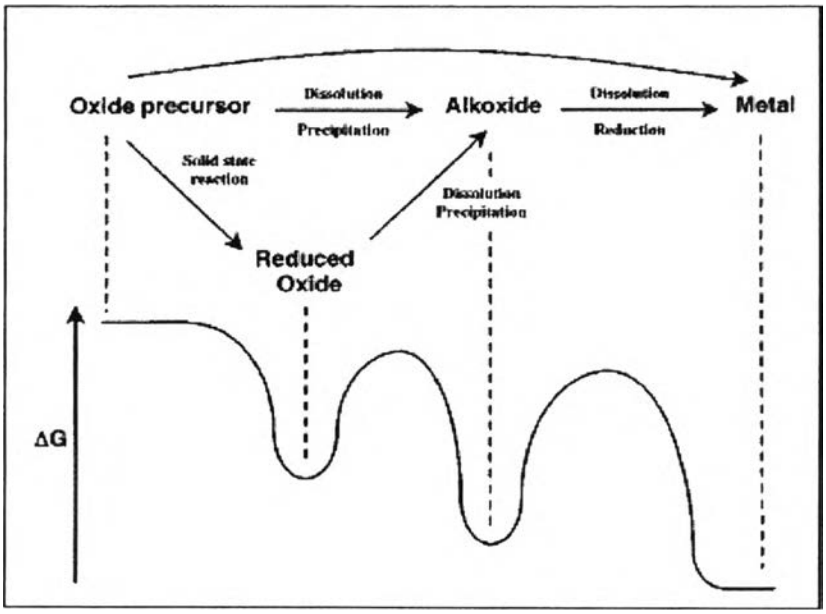


Figure 2.3 Reaction steps and intermediate phase observable during the reaction of various oxides in ethylene glycol (Larcher, 2000).

In polyol process, ethylene glycol is a widely used as a medium owing to its special physical and chemical properties. It can dissolve highly polar organics and inorganics due to its high permittivity. Moreover, its strong chelating ability, through hydroxyls as a ligand, makes it easy to form complex with transition metal ions. It can be functioned as a high boiling point solvent, reducing agent, and a stabilizer to control particle growth. This polyol process using ethylene glycol as solvent was used to synthesize 1D (Jiang, 2004; Zhang, 2009), 2D (Guo, 2006; Liu, 2010; Zhu[a], 2011) and 3D structure.

2.4 Hierarchical Structure

Hierarchical structure can be synthesized by various methods, and among the synthesis methods, the polyol process, especially ethylene glycol media, has attracted high attention. This process provides many advantages, such as the capability to control shape, size, and structure of precursor by controlling reaction temperature, reaction time, or starting materials. With the addition of surfactant, hierarchical architectures of metal oxides were obtained. A conventional surfactant, such as poly(vinyl alcohol), poly(vinyl pyrolidone) and poly(ethylene glycol), were used to control the growth of nanostructure, for example, flower-like structure of γ-Fe_2O_3 and Fe_3O_4 obtained by heating $FeCl_3$ in ethylene glycol in the presence of tetrabutylammonium bromide (TBAB). The different phases of iron oxide were obtained from different calcinations conditions using the same precursor. Heating iron oxide precursor at 450 °C for 3h in air produced α-Fe_2O_3, but under nitrogen condition it transformed to magnetite phase (Fe_3O_4) (Zhong[a], 2006).

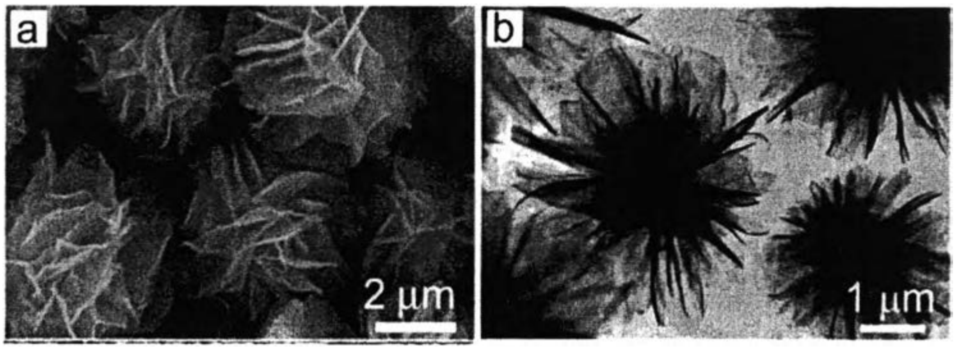


Figure 2.4 a) SEM image of the as-prepared iron oxide precursor, b) transmission electron microscopy (TEM) images of the individual flower-like structure of the iron oxide precursor (Zhong[a], 2006).

Zhong *et al.*, discussed the reaction mechanism that ethylene glycol coordinated with $FeCl_3$ first to produce iron alkoxide, in which was precipitated to become the nuclei. Followed by the secondary growth stages, the particles aggregated to form flower-like sphere through self-assembly process. This is consistent with Yang *et al.* (Yang, 2008) who prepared the flower-like luthetium oxide and proposed a functionality of ethylene glycol on the formation of 3D flower-like Lu_2O_3. They explained that the nuclei of the lutetium oxide precursor seeds were first formed through a homogeneous nucleation process, and subsequently recrystallized to grow into nanoflakes. In the presence of ethylene glycol, acting as surfactant, the ethylene glycol could be absorbed onto the flakes, leading to the self-assembly process. The schematic illustration of the flower-like formation is shown in Figure 2.5.

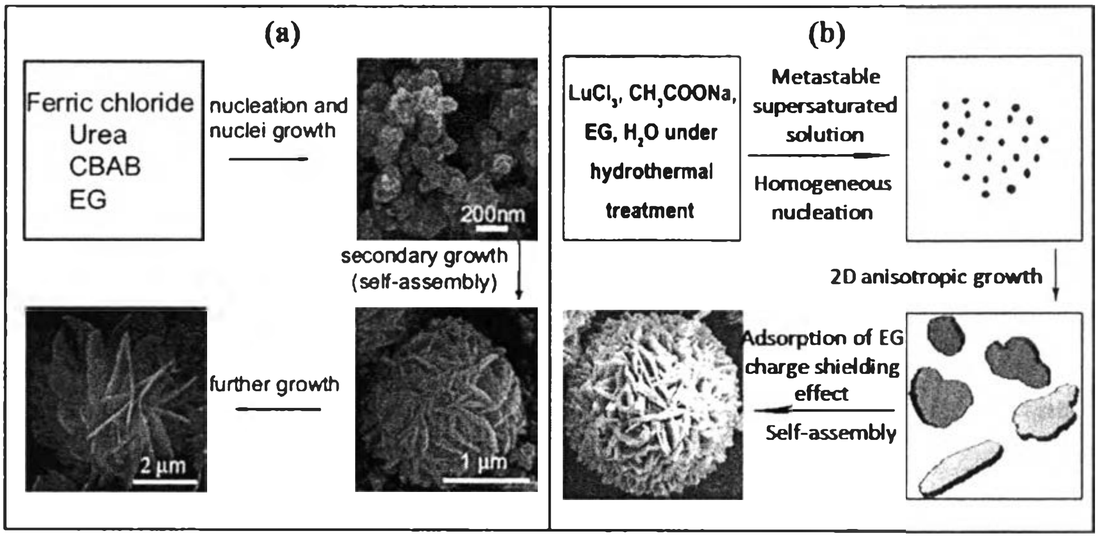


Figure 2.5 a) Schematic illustration of the morphological evolution process of a) iron oxide precursor (Zhong, 2006) and b) luthetium oxide precursor (Yang, 2008).

Cao *et al.* (Cao, 2007) received hierarchical copper oxide structure via the reaction of copper acetate with ethylene glycol (without templates, surfactant or additives) to produce organocopper. The oxide was prepared by thermal decomposition of the precursor. They obtained a "doughnut-like" structure in which the particles showed both of convex and concave surfaces. This non-classical crystallization phenomenon was observed without the employment of any polymers and surfactant. They discussed that it was the effect of a long-range dipolar control during the synthesis process. Asoka *et al.* (2009) adopted the synthesis method by using the mixture of water-ethylene glycol under hydrothermal reaction, and obtained the flower-like structure, made of 1D rods. Ma *et al.* (Ma, 2010) used the microwave-assisted method for hierarchical Bi_2O_3 sphere preparation, and with the aid of poly (vinyl pyrolidone) and microwave, the precursor was rapidly obtained within 10 min (150 °C). This microwave method was also used to prepare other metal oxides as hierarchical Fe_3O_4 microsphere in the presence of other polymers as polyethylene 2000 and polyethyleneimine instead of poly(vinyl pyrolidone) (Zhao, 2010).

This ethylene glycol mediate synthesis route is capable to prepare elemental metal as well. For example, three dimension of elemental cobalt (Figure 2.6) was prepared with the aid of hydrazine as a reducing agent (Zhang[b], 2008). They proposed the reduction mechanism of hydrazine in ethylene glycol as follows;

$$Co^{2+} + nEG \longrightarrow Co(EG)_n^{2+}$$
$$Co(EG)_n^{2+} + 3N_2H_4 \longrightarrow [Co(N_2H_4)_3]^{2+} + nEG$$
$$[Co(N_2H_4)_3]^{2+} + N_2H_4 \longrightarrow Co + 4NH_3 + N_2 + H_2 + 2H^+$$

This mechanism is related to other ethylene glycol mediated self assembly methods.

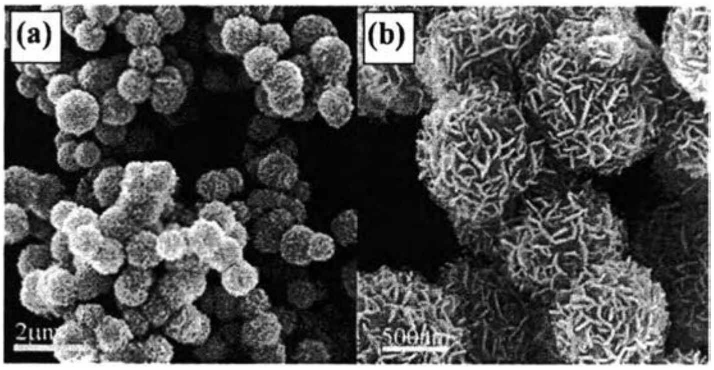
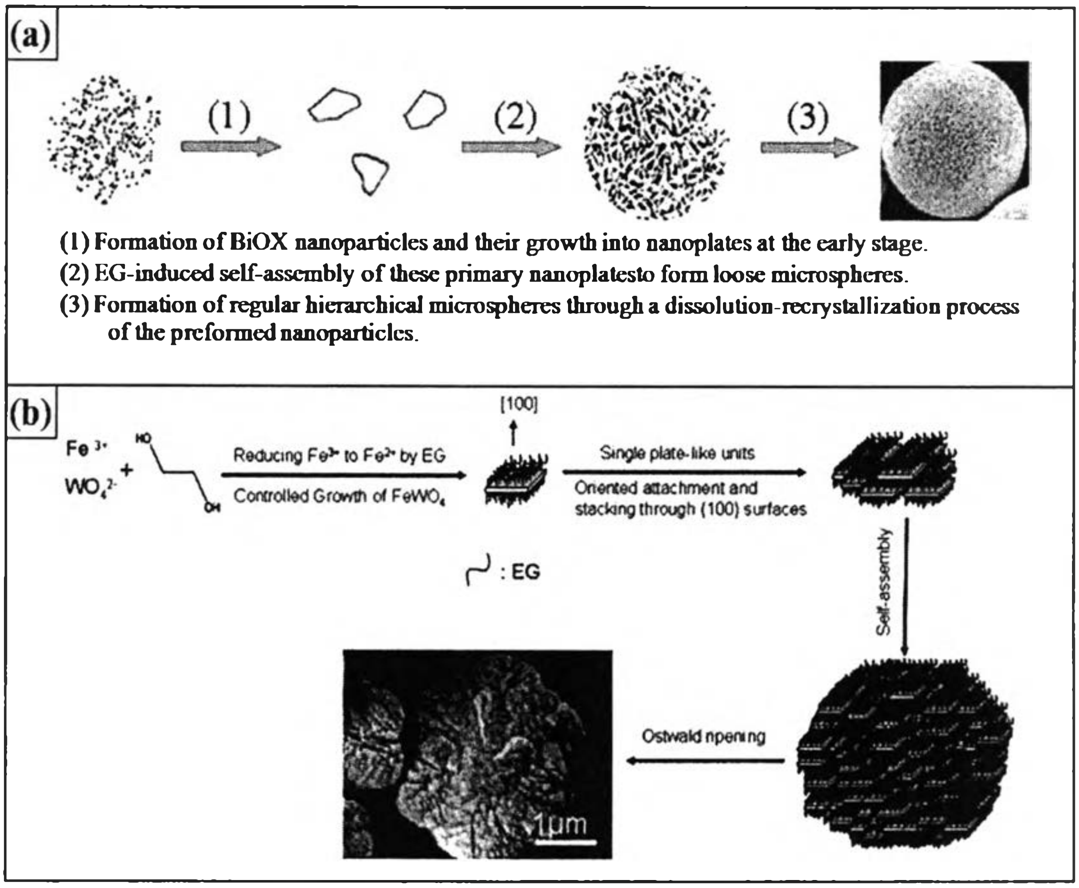


Figure 2.6 a) Low- and b) high-magnifications of FE-SEM images of the Co chains.

Hollow sphere is another type prepared by this route. For instance, Yan *et al.* prepared hollow sphere of ZnO by the reaction of zinc acetate and ethylene glycol with the help of urea (Yan, 2006). The surface subunits were easily controlled by adjusting the reaction time. The smooth microspheres began to transform into nanorod-assembled microsphere in which nanorod arrays standed perpendicular to the microsphere surface. The growth speed of the precursor nuclei was controlled via OH^- ions from urea and the coordination between the reactant and ethylene glycol. They mentioned that ethylene glycol acted as a “structure template” to effectively direct the shape of particles. Cao *et al.* (Cao, 2010) received the hollow core/shell Fe_2O_3 with different types of additives, as sodium dodecyl benzene sulfonate and urea. Moreover, Liu *et al.* (Liu, 2009) successfully prepared the magnetic nanosphere by simply heating $FeCl_3.6H_2O$ and sodium acetate.

Bimetallic compound can be prepared by this method as well. For instance, bismuth oxyhalide (BiOX, X = Cl, Br, I) was obtained ethylene glycol as solvent via one-pot solvothermal process (Zhang[a], 2008). The formation mechanism of this superstructure started from BiOX particles formed in the first stage, and the particles then grew into nanoplates assembled together to form loosely attached aggregate. When the reaction time increased, the aggregate of nanoplates continuously grew to form microsphere through a dissolution-recrystallization process of performed nanoparticles. Hierarchical $FeWO_4$ (Zhou, 2009) and CuS (Li[b], 2010) were also synthesized by the similar formation mechanism of three dimension structure, as seen in Figure 2.7.



(1) Formation of BiOX nanoparticles and their growth into nanoplates at the early stage.
(2) EG-induced self-assembly of these primary nanoplatesto form loose microspheres.
(3) Formation of regular hierarchical microspheres through a dissolution-recrystallization process of the preformed nanoparticles.

Figure 2.7 Illustration of possible formation mechanism of hierarchical structures of a) BiOX (Zhang[a], 2008) and b) $FeWO_4$ (Zhou, 2009).

In summary, ethylene glycol can be used as a medium for synthesis of 1, 2, or 3D structures of elemental metal, homometallic oxide, and bimetallic oxide. The nanostructure formation can be controlled by adjusting reaction temperature, reaction time, starting material, and chemical composition. The examples of the 3D structure preparation with and without ethylene glycol are listed in Table 2.1.

Table 2.1 Examples of hierarchical structure fabrication .

Compound	**Synthesis method**	**Structure**	**References**
Co	Reduction of cobalt choride hexanitrate in ethylene glycol and poly(vinyl pyrolidone)	Flower-like nanosphere	Zhang[b] *et al.* (2008)
Au	Reduction of silver nitrate in ethylene glycol, poly(*o*-diaminobenzene), and poly(*N*vinyl-2-pyrrolidone)	Hierarchical silver nanostrip	Guo *et al.* (2008)
CuO	Thermal decomposition of organo-copper obtained from the reaction of copper acetate and ethylene glycol.	Doughnut-like structure	Cao *et al.* (2007)
Bi_2O_3	Microwave-assisted synthesis by heating $Bi(NO_3)_3.5H_2O$ in ethylene glycol in the presence of polyvinyl pyrrolidone	Flower-like	Ma *et al.* (2010)
Bi_2WO_6	Hydrothermal heating of $Bi(NO_3)_3.5H_2O$, $Na_2WO_4.2H_2O$, and poly(vinyl pyrrolidone)	Flower-like	Li[c] *et al.* (2007)
CeO_2	Non-aqueous sol-gel method by heating $Ce(NO_3)_3.6H_2O$ in benzyl alcohol at 120 °C for 2 days	Hierarchical CeO_2 nanocrystal microsphere	Xiao *et al.* (2009)
$FeWO_4$	$FeWO_4$ microcrystals via a simple solvothermal route using $FeCl_3{\cdot}6H_2O$ and $Na_2WO_4{\cdot}2H_2O$, and CH_3COONa as precursors in ethylene glycol medium	Highly hierarchical plate-like	Zhou *et al.* (2009)

2.5 Bismuth Oxide

Generally, polymorph bismuth oxide has mainly four crystalline phases: monoclinic (α-Bi_2O_3), tetragonal (β-Bi_2O_3), faced center cubic (δ-Bi_2O_3), and body center cubic (γ-Bi_2O_3). The monoclinic phase is stable at low temperature while the faced center cubic phase is high-temperature stable. The morphology and the crystalline phase of the bismuth oxide powder rather depend on synthesis route. The transformation temperatures of polymorph bismuth oxide are shown in Figure 2.8. The monoclinic phase transforms into the cubic phase at 730 °C and melts when the temperature reaches 824 °C. If the sample was heated to temperature 730 °C or higher, the thermal hysteresis significantly affects to the phase transition. When cooling the melt of bismuth oxide to temperature 639–650 °C, the cubic phase (δ-Bi_2O_3) was formed first before transforming to the body centered cubic (γ-Bi_2O_3) or tetragonal (β-Bi_2O_3) phase, depending to the reaction condition. However, bismuth oxide phase strongly depends on the synthesis condition. For example, Tseng *et al.* (2010) successfully prepared flower-like gamma phase bismuth oxide with excellent ion conductivity. Chen *et al.* (2011) obtained the tetragonal phase of mesh-like bismuth oxide in the tetragonal phase by calcinations of the precursor at 270 °C.

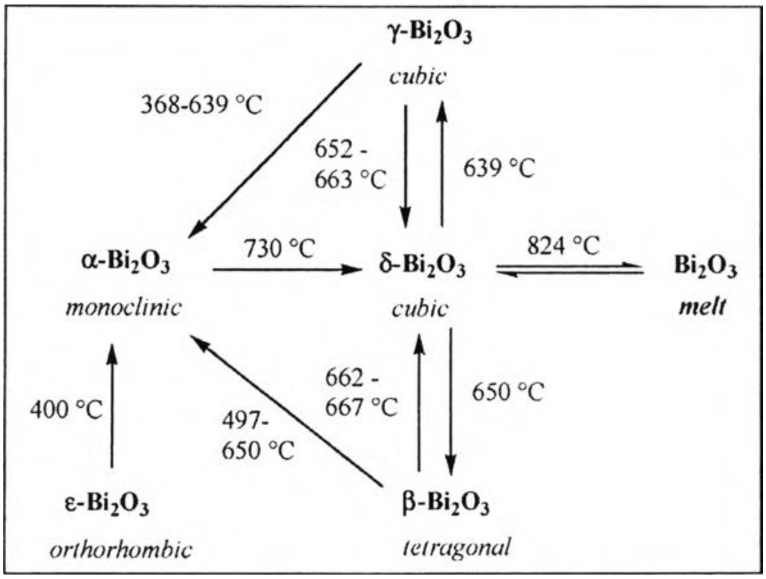


Figure 2.8 Polymorph of the phase formation of bismuth oxide.

2.6 Bismuth Titanate

2.6.1 Crystal phase of bismuth titanate

There are several phases in Bi–Ti–O system. The particular phases received more attention are $Bi_4Ti_3O_{12}$ (perovskite), $Bi_2Ti_2O_7$ (pyrochlore), $Bi_2Ti_{14}O_{11}$, $Bi_{12}TiO_{20}$ (sillenite).

(i) Perovskite: bismuth titanate ($Bi_4Ti_3O_{12}$) belongs to the Aurivillius compounds family that can be represented by the general formula of $(Bi_2O_2)^{2-}$ $(A_{m-1}B_mO3_{m+1})^{2+}$ in which A can be a monovalent (Na^+, K^+, . . .), divalent (Pb^{2+}, Ba^{2+},. . .) or trivalent (Bi^{3+}, . . .) cation or a mixture of them, B represents Ti^{4+}, Nb^{5+}, Ta^{5+}, etc., and m can have values of 2, 3, 4. In the particular case of $Bi_4Ti_3O_{12}$ ($m = 3$) its crystal structure can be described in the form of two $BiTiO_3$ unit cells of hypothetical perovskite structure interleaved with $(Bi_2O_2)^{2+}$ layers (Aurivillius, 1949). The compound is monoclinic ($C_{1h} = m$) at room temperature, and turns into tetragonal (D_{4h} = 4mmm) above the Curie temperature (675 °C). $Bi_4Ti_3O_{12}$ has been studied by various investigators for its ferroelectric, piezoelectric, and electro-optic switching behavior (Dorrain *et al.*, 1971; Billegas *et al.*, 1996)

(ii) Pyrochlore; it is a material of the type $A_2B_2O_6$ and $A_2B_2O_7$ where the A and B species are generally rare-earth or transition metal species. The pyrochlore oxides show many interesting properties, such as ionic conduction, electronic conduction, catalytic activity, and fluorescence. The additional anion vacancy resides in the tetrahedral intersticy between adjacent B-site cations. The crystal structure for the $A_2B_2O_7$-type-pyrochlore has octahedrallly coordinated B-site cations, 8-coordinated A-site cation, and two distinct oxygen sites. The crystal structure of perovskite, ABO_3, also has octahedrally coordinated B-site cations, and 12-coordinated A-site cations. The crystal structure of the pyrochlore-perovskite shares several features, such as BO_6 octahedra (Speakman *et al.*, 2004). Small, localized regions of pyrochlore-type ordering were also observed in the perovskite materials (Irvine, 2003).

(iii) Sillenite: $Bi_{12}TiO_{20}$ belongs to a family of sillenite compounds. Sillenites with the structure of the metastable cubic γ-Bi_2O_3 (space group I23) are a well-known group of non-centro-symmetric crystals (Żmija, 2002; Kityk, 2004).

Sillenites are formed during reaction of Bi_2O_3 with many metallic and non-metallic oxides of Ge, Si, Ti, Pb, Ga, B, etc, mainly in a 6:1 molar ratio (Kityk, 2004). The family of sillenite compounds has the general formula of $Bi_{12}MO_{20}$ where M represents a tetravalent ion or a combination of ions, which gives an average charge of 4+. The framework of the $Bi_{12}TiO_{20}$ crystal structure is formed by Bi–O polyhedra, in which Bi ions are coordinated to five oxygen ions in an octahedral arrangement together with the stereochemically active $6s^2$ electron lone pair of Bi^{3+}. The Bi-O polyhedron network connects to geometrically regular TiO_4 tetrahedra. Each tetrahedron is formed by four oxygen anions with the Ti cation, occupying the tetrahedral interstice. Sillenites have very good photorefractive, electro-optic, piezoelectric, and photochromic properties. They can be used in signal processing and optical memories for data storage (Żmija, 2002).

2.6.2 Phase transformation of Bi_2O_3-TiO_2 system

Bi_2O_3–TiO_2 system has several crystal phase structures, such as sillenite, perovskite, or pyrochlore. The phase diagram and the transformation of each phase has been widely discussed and investigated. Navarro-Rojero (2010) studied the intermediate phase formation during the synthesis of $Bi_4Ti_3O_{12}$ by solid state reaction. The phase of bismuth titanate was measured by X-ray diffraction pattern and Raman spectroscopy. They used Bi_2O_3 and TiO_2 as raw materials. The $Bi_4Ti_3O_{12}$ formation passed through an intermediate of $Bi_{12}TiO_{20}$ sillenite phase which formed at temperatures over 300 °C. This sillenite phase is stable up to 750 °C. However, in the presence of TiO_2, $Bi_{12}TiO_{20}$ transformed to $Bi_4Ti_3O_{12}$ at temperatures >500 °C (Navarro-Rojero, 2010).

$$6Bi_2O_3 + 9TiO_2 \longrightarrow Bi_{12}TiO_{20} + 8TiO_2 \longrightarrow 3Bi_4Ti_3O_{12} \qquad (3)$$

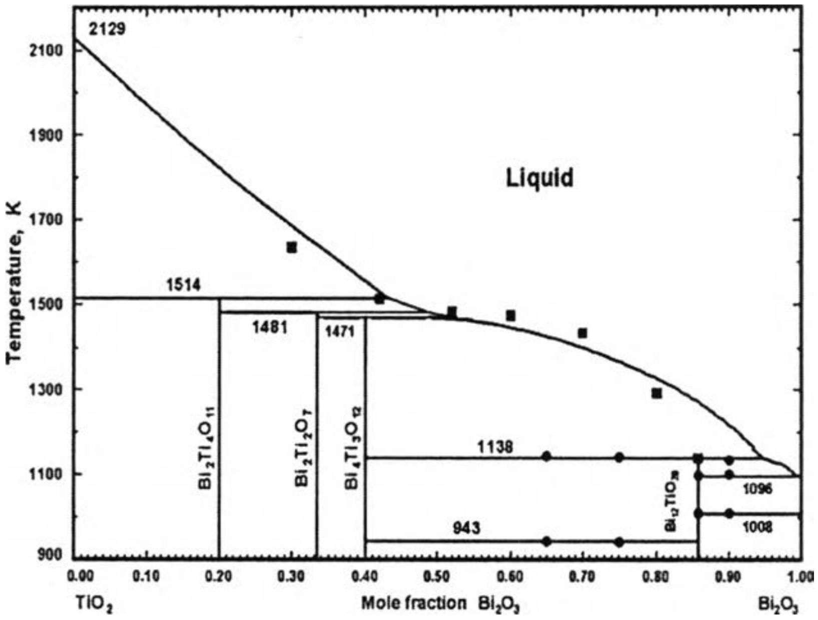


Figure 2.9 Bi_2O_3-TiO_2 phase diagram (Masuda, 1992, and Lopez-Martinez, 2010).

Comparing Masuda *et al.* and Lopez-Martinez works, the perovskite phase formation passed through the sillenite phase. According to Lopez-Martinez's results, the only two intermediate compounds in the Bi_2O_3 rich region were $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$. The $Bi_4Ti_3O_{12}$ phase presents the well-known plate-like morphology (Lopez-Martinez, 2010).