

Research Article

Low Temperature Synthesis of Hexagonal Shaped α -Al₂O₃ Using a Solvothermal Method

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Received 15 November 2012; Revised 6 December 2012; Accepted 12 December 2012

Academic Editor: Jianxin Zou

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This study demonstrates the low temperature synthesis of α -Al₂O₃ by solvothermal method using gibbsite alumina precursor in 1, 4-butanediol solvent according to various pH conditions. In acidic solution, an orthorhombic boehmite (AlOOH) structure was obtained after solvothermal reaction. A significant result in this study was that the solvothermally synthesized alumina in pH = 9 at 300 °C for 36 h represented a rhombohedral α -Al₂O₃ structure hexagonal shaped with about 1.5~2.0 μ m of particle size. Otherwise, the α -Al₂O₃ structure was rather changed to the mixture of a boehmite and α -Al₂O₃ structures above pH = 11. In the case of α -Al₂O₃ synthesized at pH = 9, the specific surface area was 26.18 m²/g, and the particles that were stable in acidic solution resulted in 61.80 mV of zeta potential.

1. Introduction

The α -Al₂O₃ powder has considerable potential for a wide range of applications including high strength materials, sapphire crystal growth, electronics, semiconductors, and catalysts [1–4]. In particular, the current high demand for sapphire substrates for the LED market has greatly added to the crystal growth business on top of existing applications. The volume of sapphire wafer production is currently measured in hundreds of millions of units annually. Here α -Al₂O₃ crystals have attracted attention as a source of sapphire. Due to its versatility, increasing interest has focused on the synthesis of α -Al₂O₃. Conventional synthesis processes of α -Al₂O₃ involve vapor phase reaction, precipitation, sol-gel, hydrothermal, and combustion methods. Vapor phase reaction for preparation fine α -Al₂O₃ powder from a gas phase precursor demands high temperature above 1200°C [5]. The precipitation method suffers from its complexity and time consuming as like long washing times and aging time [6]. The direct formation of α -Al₂O₃ via the hydrothermal method needs high temperature and pressure [7].

The combustion method has been used to yield α -Al₂O₃ powders, whereas the powder obtained from the process is usually hard aggregated but contains nano-sized primary particles [8]. Sol-gel a commonly from a precursor solution used technique, involves the formation of an amorphous gel; however, this method needs some thermal treatment steps at various temperatures [9, 10]. In general, α -Al₂O₃ derived from the decomposition of gelatinous boehmite, gibbsite, and related hydroxide alumina undergoes a number of transitional phases. Amorphous alumina dehydrates at 500°C to form γ -alumina which then transforms to δ -alumina and θ -alumina before becoming α -Al₂O₃ in the range of 1,200~1,400°C, depending on the procedure [11]. Recently several studies on the preparation of α -Al₂O₃ have tried to lower the formation temperature by using additives [12, 13]. It has been suggested that the metal-organic-derived alumina could lower the transformation temperature of α -Al₂O₃. In our previous researches [14, 15], we have also reported two papers; both were about mild temperature synthesis of α -Al₂O₃ using a chelating reagent as like ethylenediamine and a pre-microwave treatment,

resulted that α - Al_2O_3 structure was successfully obtained below $1,000^\circ\text{C}$. However, the crystallization temperature is still high. Therefore, new methods are needed to overcome the problem. In particular, the solvothermal method is an alternative to calcinations for promoting crystallization under mild temperatures. This process has been applied recently to the synthesis of small ceramic particles and films containing a range of metal oxides. Solvothermal treatments can be used to control the grain size, particle morphology, crystalline phases, and surface chemistry by regulating the sol composition, reaction temperatures, pressure, solvent nature, additives, and aging time. The particles prepared using the solvothermal method are expected to have a larger surface area, smaller particle size, and greater stability than those obtained by other methods, such as the sol-gel method. There are few reports of α - Al_2O_3 , which are prepared using the solvothermal method. Bell and Adair [16] have synthesized α -alumina in 1,4-butanediol solvent by reaction of gibbsite powder at 300°C for 36 h under a stirring rate of 460 rpm and autogenously pressures. They have also controlled the morphology through the use of special adsorbents in non-aqueous solution synthesis involves consideration of solvent degradation. Such studies are continuing, but without evident success as yet.

In this study, we have also tried to synthesize a special α - Al_2O_3 powder as a raw material for sapphire crystal growth in application to the LED industry. The α - Al_2O_3 structure in this study is controlled according to the effects of the pHs in the preparation step using a solvothermal method. The as-synthesized Al_2O_3 powders are characterized by X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), specific surface areas (Brunauer-Emmett-Teller, BET), X-ray photoelectron spectroscopy (XPS), and zeta potentials using electrophoresis light scattering (ELS) measurements.

2. Experimental

A solvothermal method was introduced in this study [16]. Gibbsite ($\text{Al}(\text{OH})_3$, sigmaaldrich.com/sigma-aldrich/home.html) was used as an aluminum precursor. First, the Gibbsite of 10.0 g was well dispersed in small amount of methanol with sonification for 1 h and then the colloidal solution was well mixed with excess 1,4-butanediol solvent for 2 h. The colloidal solution was thermally treated at 70°C for 24 h to remove methanol. Then acetic acid or ammonia water was slowly dropped into the solution to control pH = 4, 7, 9, and 11. The final solution was stirred homogeneously for 5 h, and then the solution was moved to a liner in autoclave, and finally the autoclave was heated in N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$ to 300°C and then maintained isothermally at this temperature for 36 h and 70 atm. After solvothermal treatment, the obtained white powders were washed and dried. The synthesized Al_2O_3 were named to pH 4, 7, 9, and 11 according to pH of the final solution in the preparation step.

The as-synthesized Al_2O_3 powders were identified using powder XRD (model MPD, PANalytical, Yeungnam University Instrumental Analysis Center, Korea) with nickel-filtered $\text{CuK}\alpha$ radiation (30 kV, 30 mA) at 2-theta angles of 10 – 90° . The scan speed was $10^\circ/\text{min}$, and the time constant was 1 s. The sizes and shapes of the materials were measured by field emission SEM/energy-dispersive X-ray spectroscopy (FESEM/EDS; S-4100, Hitachi, Yeungnam University Instrumental Analysis Center, Korea). XPS measurements of the binding energy of Al_{2p} and O_{1s} orbitals in alumina powders were recorded with a model AXIS-NOVA (Kratos Inc., Korea Basic Science Institute Jeonju Center, Korea) system, equipped with a nonmonochromatic $\text{AlK}\alpha$ (1486.6 eV) X-ray source. The specific surface area was calculated according to the BET theory that gives the isotherm equation for multilayer adsorption by generalization of Langmuir's treatment of the unimolecular layer. The BET surface areas were measured using a Belsorp II instrument. The materials were degassed under vacuum at 120°C for 1 h before the BET surface measurements. Then the samples were thermally treated at 300°C for 30 min. The BET surface areas of the materials were measured through nitrogen gas adsorption using a continuous flow method with a mixture of nitrogen and helium as the carrier gas. The zeta potentials of the materials were determined by electrophoretic mobility using an electrophoresis measurement apparatus (ELS 8000, Otsuka Electronics, Japan) with a plate sample cell. ELS determinations were performed in the reference beam mode at a laser light source wavelength of 670 nm, modular frequency of 250 Hz, and scattering angle of 15° . The standard error of the zeta potentials, converted from the experimentally determined electrophoretic mobility, was typically $< 1.5\%$ and the percent error $< 5\%$. To measure the zeta potentials, 0.1 wt% of each sample was dispersed in deionized water and the pH of the solution was adjusted to 7. Relative sintered particle size distributions of the various pH solutions were also measured by using this equipment. Thermal gravimetric analysis measurements were collected using a TGA N-1000 (Scinco, Korea) thermal gravimetric analysis (TGA) equipped with a platinum crucible. Samples were heated from room temperature ($\sim 50^\circ\text{C}$) to 900°C with a heating rate of 5°C min^{-1} while the chamber was continuously purged with O_2 gases at a rate of 25 mL/min.

3. Results and Discussion

Figure 1 shows the XRD patterns of the four types as-synthesized Al_2O_3 powders according to various pH conditions after solvothermal treatment at 300°C for 36 h. The synthesized Al_2O_3 powder at pH = 4 exhibited peaks at 2 theta angles of 14.51, 28.22, 38.44, 49.18, 49.47, 55.19, 63.93, and 72.03° corresponding to the (d_{020}), (d_{120}), (d_{031}), (d_{200}), (d_{200}), (d_{220}), (d_{231}), and (d_{251}) spaces, respectively, and they were ascribed to the orthorhombic boehmite (AlOOH) structure [17]. However, the structures changed to the boehmite/ α - Al_2O_3 mixture at pH = 7. A significant result showed at pH = 9 that the XRD peaks assigned to α - Al_2O_3 were clearer and sharper without high thermal

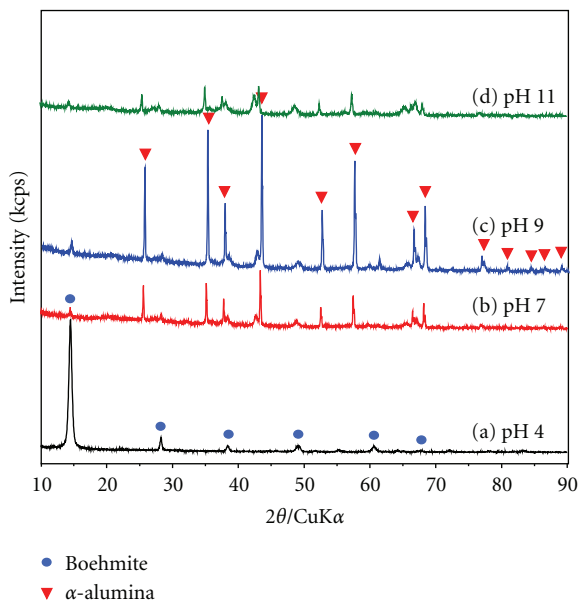


FIGURE 1: The XRD patterns of the Al_2O_3 powders as-solvothermally synthesized according to pHs.

treatment above $1,000^\circ\text{C}$. The synthesized $\alpha\text{-Al}_2\text{O}_3$ particle exhibited peaks at 2 theta angles of 25.57, 35.14, 37.76, 43.33, 46.16, 52.53, 57.47, 61.27, 66.49, 68.18, and 76.84, corresponding to the (d012), (d104), (d110), (d113), (d202), (d024), (d116), (d018), (d214), (d300) and (d1,0,10) spaces, respectively [18]. It was ascribed to the rhombohedral structure. Consequently, $\alpha\text{-Al}_2\text{O}_3$ was easily acquired with the solvothermal process, and it lowered the existing temperature by $500\sim 900^\circ\text{C}$, compared to the sol-gel process. These results revealed the pH effect on the crystallinity because of hydrolysis and poly-condensation in solvothermal treatment. This indicates that the rate of hydrolysis is governed by the hydronium ion in acidic solutions, so that the amount of water is small due to rapid formation of H_3O^+ . On the other hand, the reaction is controlled by the hydroxyl ions (OH^-) when powders are derived at $\text{pH} = 9$. The initial growth leads to a linear chain, but the high concentration of OH^- ions leads to crystallization because the probability of intermolecular reaction is higher than the intra-molecular reaction. The most probable metal-oxygen polymeric network, formed at high pH. The full width at half maximum (FWHM) height of the peak at $2\theta = 35.14^\circ$ (104) was measured, and the Scherrer equation [19], $t = 0.9\lambda/\beta \cos \theta$, where λ the wavelength of the incident X-rays, β , the FWHM in radians and θ the diffraction angle, was used to determine the crystalline domain size. The calculated crystalline domain size based on a special peak of 35.14° (d104) is 39.66 nm for the $\alpha\text{-Al}_2\text{O}_3$ powders synthesized at $\text{pH} = 9$.

TEM and SEM images of the solvothermally synthesized Al_2O_3 particles prepared at various pHs are shown in Figure 2. This figure revealed that the shapes varied according to the pH. At lower pH, the Al_2O_3 powder was close

to an orthorhombic rectangular shape. However, at neutral solution, the form was changed to cube/hexagonal mixture shape. In particular, it was transferred the $\alpha\text{-Al}_2\text{O}_3$ structure to the perfect hexagonal-shaped at $\text{pH} = 9$, and eventually it became huge square pillars of $1.5\sim 2.0\ \mu\text{m}$. However at higher pH, the shape was seemed to collapse.

The atomic compositions on the surface of the synthesized $\alpha\text{-Al}_2\text{O}_3$ powders were analyzed by EDS and the results are summarized in Table 1, which revealed the presence of Al and O as the only elementary components of two samples with an Al:O atomic ratio of about 6:4. In the samples synthesized in acidic solutions, the measured Al:O ratio revealed a little higher aluminum content than that in alkali solution of $\text{pH} 11$ in this study. However, at $\text{pH} = 9$ that represented $\alpha\text{-Al}_2\text{O}_3$ structure, the oxygen concentration was higher compared to the other phase's alumina.

Figure 3 presents the high-resolution spectra obtained from the quantitative XPS analyses of the as-synthesized four Al_2O_3 samples produced at various pHs. The survey spectra of materials contained Al_{2p} and O_{1s} peaks by XPS handbook [20]. It is well known that the $\text{Al}_{2p_{3/2}}$ orbital in α -type Al_2O_3 has a binding energy of $73.5\sim 74.2\ \text{eV}$, and this was assigned to Al^{3+} in Al_2O_3 and was almost same in $\text{pH} 4, 7, 9$, and 11 , which gave an $\text{Al}_{2p_{3/2}}$ orbital binding energy of $72.85\sim 73.29\ \text{eV}$. In general, a large binding energy indicates the presence of more oxidized states. In this study, the $\text{Al}_{2p_{3/2}}$ orbital binding energies were shifted to lower binding energy compared to the pure α -type Al_2O_3 represented in XPS handbook, which were assigned to reduced Al ions in Al_2O_3 . The O_{1s} region was decomposed into two contributions: metal-O ($\sim 530.2\ \text{eV}$) in the metal oxide and metal-OH ($531.0\ \text{eV}$). In general, a higher metal-OH peak indicates that particles are more hydrophilic. However, only a single peak was seen in all samples induced from $\text{pH} 4, 7, 9$, and 11 , at around $531\sim 532\ \text{eV}$, which was assigned to Al-O.

The BET surface areas of the materials were measured by nitrogen gas adsorption using a continuous flow method with a mixture of nitrogen and helium as the carrier gas. The pore size distribution is an important characteristic for porous materials. The relative pressure at which pore filling takes place by capillary condensation can be calculated from Kelvin's equation. By using Kelvin's equation, the pore radius in which the capillary condensation occurs actively can be determined as a function of the relative pressure (P/P_0). The mean pore diameter, D_p , was calculated from $D_p = 4VT/S$, where VT is the total volume of pores, and S the BET surface area. All isotherms belonged to type I-V according to the IUPAC classification [21]. The adsorption-desorption isotherms of N_2 at $77\ \text{K}$ for the four Al_2O_3 powders, were calculated as shown in Figure 4, and the values are also summarized in the table. All of Al_2O_3 samples in this study showed isotherms belong to III type in the IUPAC classification [22]. The synthesized Al_2O_3 samples in this study did not have any pores and however the BET surface area and pore volume were decreased in Al_2O_3 sample synthesized at $\text{pH} = 9$ to $26.18\ \text{m}^2\ \text{g}^{-1}$ and $0.249\ \text{cc/g}$, respectively, compared to the other Al_2O_3 samples. We expected from this result that the α -type Al_2O_3 derived from $\text{pH} = 9$ has a larger particle size and higher density.

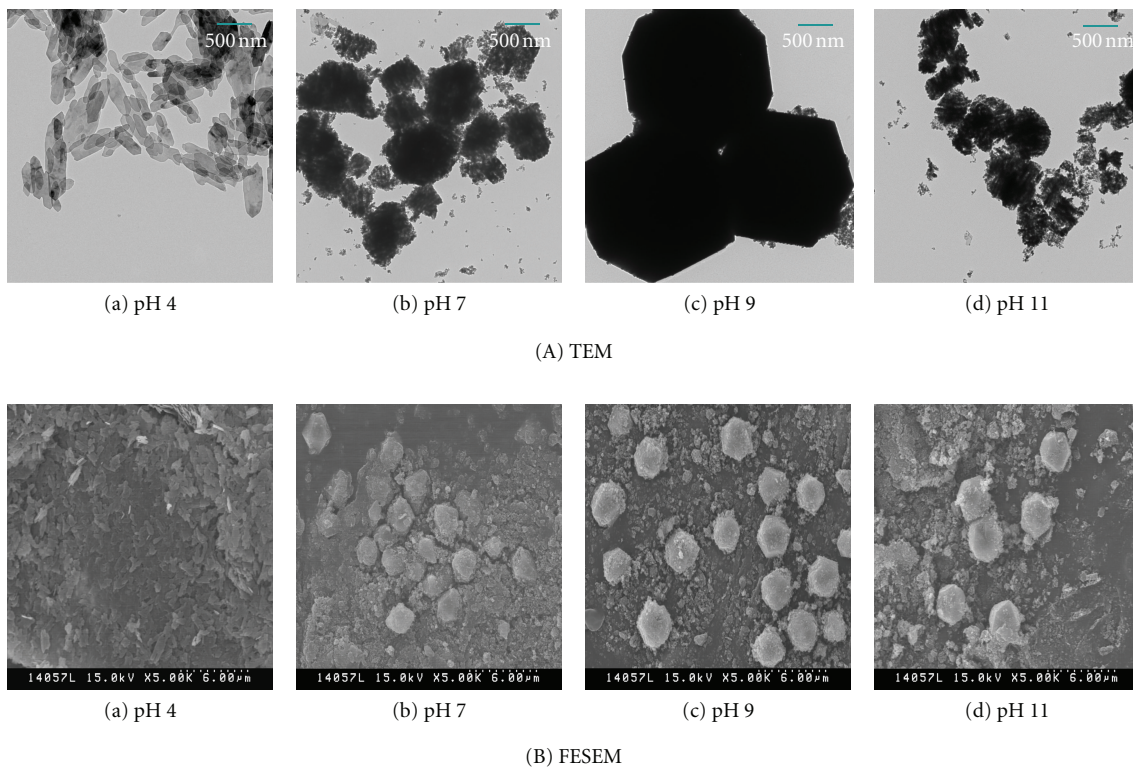


FIGURE 2: The TEM and FESEM images of the Al_2O_3 powders as-solvothermally synthesized according to pHs.

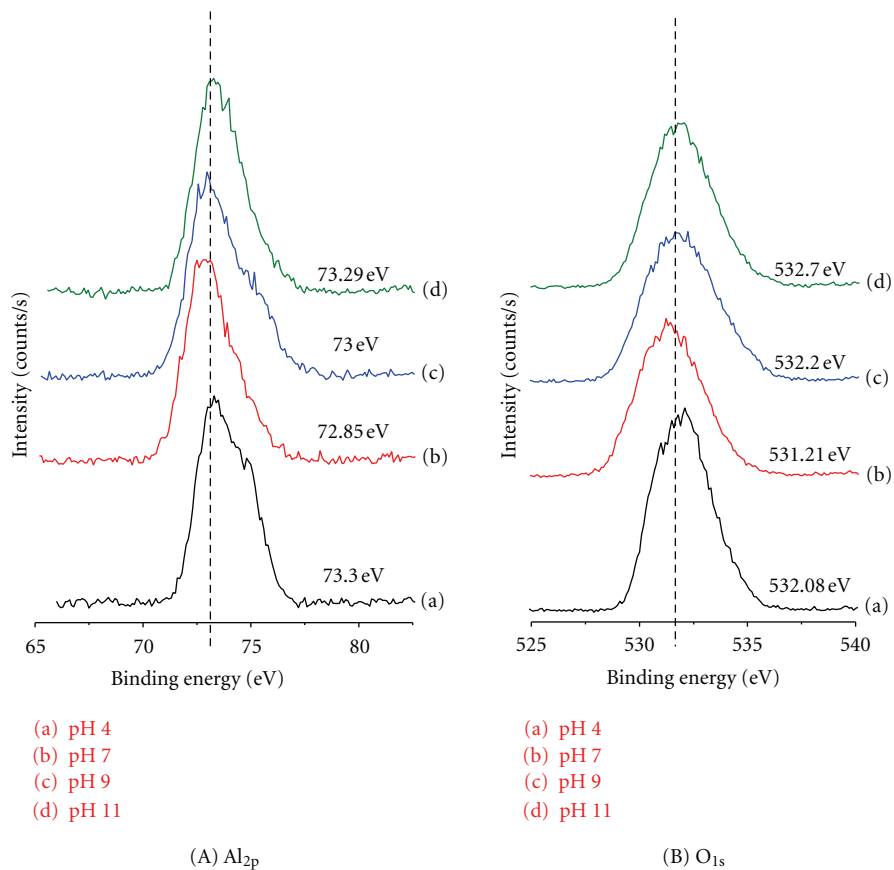
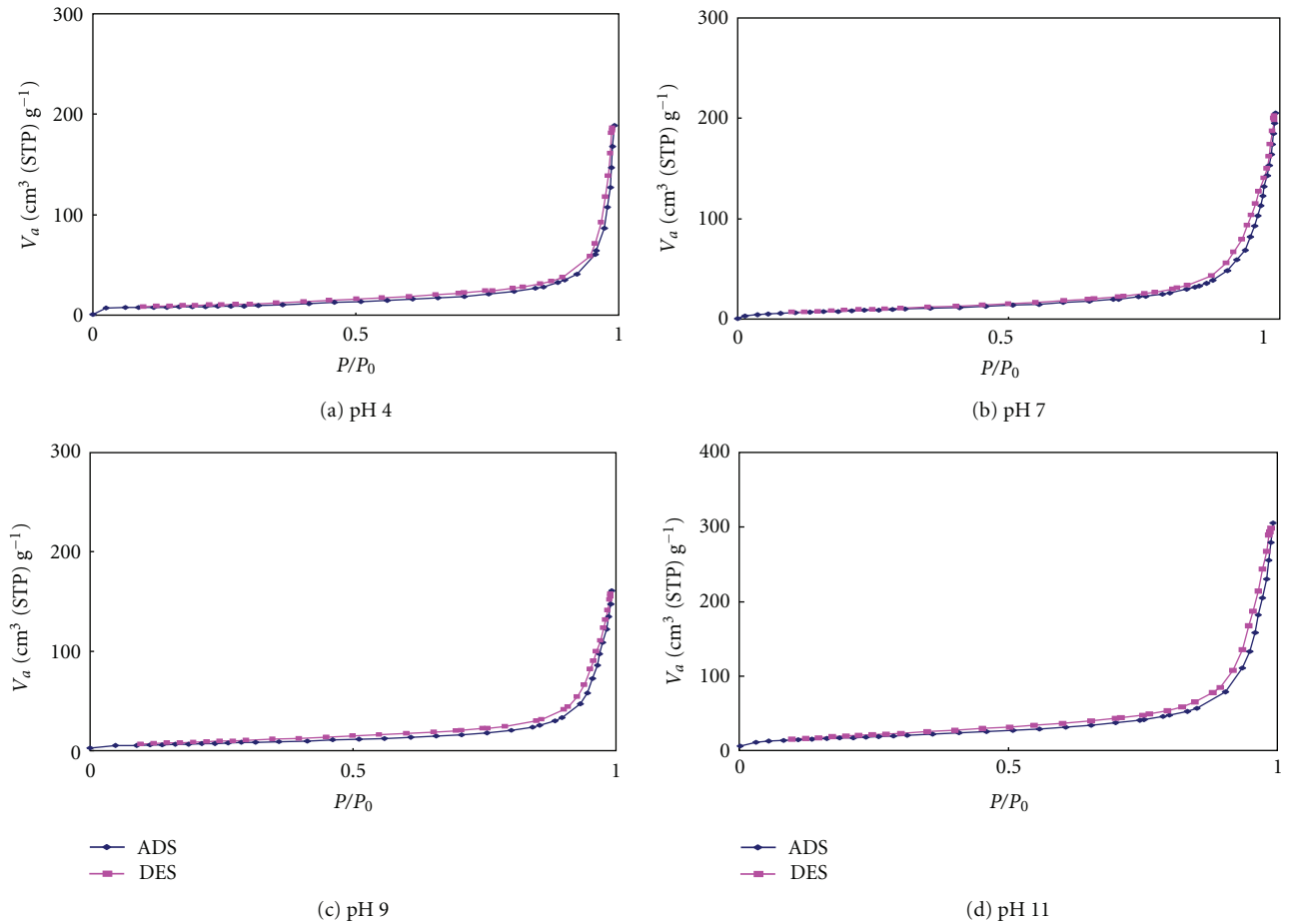


FIGURE 3: The XPS curves of the Al_2O_3 powders as-solvothermally synthesized according to pHs.



Samples	BET multipoint surface area (m ² /g)	Total pore volume (cc/g)	Bulk pore diameter (nm)
pH 4	28.02	0.292	41.69
pH 7	31.68	0.317	40.08
pH 9	26.18	0.249	37.99
pH 11	63.02	0.471	29.92

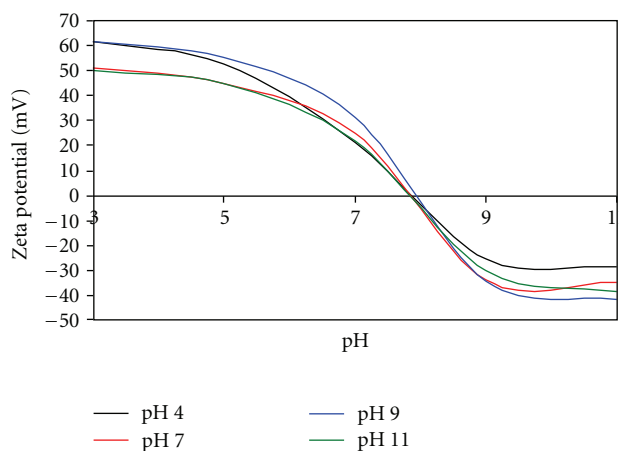
FIGURE 4: The adsorption-desorption isotherm curves of N₂ at 77 K on the Al₂O₃ powders as-solvothermally synthesized according to pHs.

TABLE 1: The atomic compositions analyzed by energy-dispersive X-ray spectroscopy (EDS) study on the Al₂O₃ powders as-solvothermally synthesized according to pHs.

Samples elements	pH 4		pH 7		pH 9		pH 11	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
O	55.89	68.12	49.37	62.19	45.79	58.76	51.15	63.85
Al	44.11	31.88	50.63	37.81	54.21	41.24	48.85	36.15
Total	100		100		100		100	

The zeta potential is an important parameter in colloidal stability, since it reflects the variation in surface potential for a specific material. These powders were derived from the solution route at low temperature; therefore, zeta potential studies were conducted to understand the surface charge

of these powders. Figure 5 shows the zeta potential data of an aqueous suspension of synthesized Al₂O₃ powders. No electrolyte was added to control the ionic strength of the solutions. The zeta potentials of all of the Al₂O₃ suspensions were significantly decreased with increasing pH. The surface



Samples pHs	pH 4		pH 7		pH 9		pH 11	
	A	B	A	B	A	B	A	B
pH = 3	61.49	797.3	51.06	1341.6	61.80	1893.4	50.10	1144.1
pH = 5	52.84	854.4	44.59	1418.7	55.26	2015.9	45.04	1378.5
pH = 7	21.28	1906.5	25.16	1681.4	31.14	2555.0	21.64	3997.4
pH = 9	-25.31	1051.7	-33.58	1581.6	-34.16	2319.5	-29.88	1934.4
pH = 11	-28.31	960.8	-34.99	1414.2	-41.60	2184.9	-38.49	1838.1

* A: zeta potential (mV) and B: aggregated particle size (nm) in aqueous solution.

FIGURE 5: The zeta potential data of an aqueous suspension of the Al_2O_3 powders as-solvothermally synthesized according to pHs.

charges were transferred from positive in acidic solution to negative in alkali solution. For $\alpha\text{-Al}_2\text{O}_3$ synthesized at pH = 9, the isoelectric point was at pH = 8 with large aggregation, and it positively charged to a maximum of 61.80 mV at pH = 3, which indicated that the $\alpha\text{-Al}_2\text{O}_3$ colloidal existed stably while having a small aggregation. Above this pH, the positive charge of the $\alpha\text{-Al}_2\text{O}_3$ particle was decreased with the same trend of mobility, resulting in an average aggregated diameter of 2,555 nm at pH = 7.

4. Conclusions

This study demonstrated the effect of pH in solvothermal synthesis to reduce the crystal growth temperature of $\alpha\text{-Al}_2\text{O}_3$ compared to ordinary methods. Most significantly, the solvothermal treatment produced rhombohedrally structured $\alpha\text{-Al}_2\text{O}_3$ with the hexagonal particle range of 1.5~2.0 μm at 300°C with pH = 9 and however the boehmite and mixed structures were seen at pH = 4, 7, and 11. The surface area was smaller in $\alpha\text{-Al}_2\text{O}_3$ synthesized at pH = 9. Electrophoretic light scattering (ELS) measurement in aqueous solution at pH = 3 revealed positive surface charges in the $\alpha\text{-Al}_2\text{O}_3$, which indicated that the $\alpha\text{-Al}_2\text{O}_3$ colloidal existed stably while having a small aggregation.

Acknowledgments

This research was financially supported by the Ministry of Education, Science and Technology (MEST) and National

Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation.

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