Synthesis and Characterization of Y_2O_3 Powders by a Modified Solvothermal Process

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Abstract Y_2O_3 nanomaterials have been widely used in transparent ceramics and luminescent devices. Recently, many studies have focused on controlling the size and morphology of Y_2O_3 in order to obtain better material performance. Y_2O_3 powders were prepared under a modified solvothermal condition involving precipitation from metal nitrates with aqueous ammonium hydroxide. The powders were obtained at temperatures at 250°C after a 6h process. The properties of the Y_2O_3 powders were studied as a function of the solvent ratio. The synthesis of Y_2O_3 crystalline particles is possible under a modified solvothermal condition in a water/ethylene glycol solution. Solvothermal processing condition parameters including the pH, reaction temperature and solvent ratio, have significant effects on the formation, phase component, morphology and particle size of yttria powders. Ethylene glycol is a versatile, widely used, inexpensive, and safe capping organic molecule for uniform nanoparticles besides as a solvent. The characterization of the synthesized Y_2O_3 powders were studied by XRD, SEM (FE-SEM) and TG/DSC. An X-ray diffraction analysis of the synthesized powders indicated the formation of the Y_2O_3 cubic structure upon calcination. The average crystalline sizes and distribution of the synthesized Y_2O_3 powders was less than 2 μm and broad, respectively. The synthesized particles were spherical and hexagonal in shape. The morphology of the synthesized powders changed with the water and ethylene glycol ratio. The average size and shape of the synthesized particles could be controlled by adjusting the solvent ratio.

Key words Y_2O_3 powder, modified solvothermal process.

1. Introduction

Yttrium oxide (Y_2O_3) is an important engineering materials in many fields due to its chemical and physical properties, such as high permittivity,¹⁾ high melting point, a relatively large band gap energy etc. Y_2O_3 nanomaterials have been widely used in transparent ceramics and luminescent devices. Recently there are many studies focusing on controlling the size and morphology of Y_2O_3 in order to obtain better materials performance. For example, Y_2O_3 could be used as a waveguide material due to its high refractive index, or as a buffer layer for ferroelectrics and superconductors because of its low lattice-mismatch with silicon.²⁾ Yttria finds many high technology applications due to its excellent high affinity for oxygen and sulfur and well-defined crystal structures, whose properties can be tailored by incorporating different types of ions into the structure.^{3,4)} Yttria is used as a host matrix for phosphors used in televisions and also in synthesis of yttria-thoria type translucent ceramics for lasers. Yttria is also being tried as a mould coating for precision

Ti-6Al-4V castings.⁵⁾ In view this, yttria still attracts researchers for developing newer and better routes for its preparation in nano-crystalline range.

In recent years, nanocrystals have attracted researchers interest because of their unusual behavior.^{6,7)} Rare earth related nanocrystals,^{8,9)} especially the nanosized yttrium oxide(Y_2O_3) with controllable size and morphology, which may have better sintering ability and unique luminescent property, have been widely studied because of their potential applications in transparent ceramics and luminescent devices,^{10,11)} such as FED and CRT, etc. For example, $Y_2O_3:Eu^{3+}$ is the prominent red emitting phosphor with high luminescence quantum efficiency, and widely used in lamps and display, Y_2O_3 also can be used as advanced ceramics,^{12,13)} superconductor,¹⁴⁾ insulator¹⁵⁾ and sensor.¹⁶⁾ Y_2O_3 nanostructures such as nanotubes,¹⁷⁾ nanowires,¹⁸⁾ nanorods,¹⁹⁾ nanobelts,^{20,21)} nanodisks²²⁾ and nanosheets²³⁾ have been prepared. However, the synthesis and self-assembly of Y_2O_3 microstructures have been rarely reported.

Various Chemical routes such as spray drying,²⁴⁾ co-precipitation²⁵⁾ and sol-gel²⁶⁾ are known to yield sinter-active materials. Yttria powders obtained after thermal decomposition of yttrium precursors at high temperatures (carbonates, oxalate, nitrate and hydroxide) require tempera-

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tures in excess of 1873K for sintering.²⁷⁾

Among the many different methods listed above, Hydrothermal processes have a potential for the direct preparation of crystalline ceramic powders and offer a low temperature alternative to conventional powder synthesis techniques in the production of oxide powders.²⁸⁾ This technique can produce fine, high purity, stoichiometric particles of single and multicomponent metal oxides.²⁹⁾ Furthermore, if the process conditions such as solution pH, solute concentration, reaction temperature, reaction time, seed materials, and the type of solvent are carefully controlled, ceramic particles of the desired shape and size can be produced.³⁰⁾

The objective of this study is to prepare the yttria powders by a modified solvothermal process, and to investigate the effects of the processing conditions on the formation, morphology, size and phase of the powders.

2. Experimental Procedure

The preparation sequence of yttria powder is schematically illustrated in Fig. 1.

Yttrium Nitrate (99.99%, DAE JUNG, Korea) was dissolved with 100 ml deionized water to the concentration of 0.2M. Yttria precursors were precipitated from 0.2M solution by slowly adding NH_4OH with rapid stirring in which the pH of starting solutions varied between 7 and 11. The precipitated yttria precursors were washed by respected cycles of centrifugation and re-dispersion in water. Washing was performed for a minimum of two times in water and

three times in ethanol. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in adequately ratio of the water/ethylene glycol under vigorous stirring. After that the colloidal mixture was transferred into a 1000 ml stainless steel autoclave and sealed.

The autoclave was then heated to the 250°C at a rate of 5°C/min for 6h. The reaction products were washed at least five times by repeated cycles of centrifugation and re-dispersion in ethanol and D.I. Water. The characterization of the recovered powders was observed using X-Ray Diffraction (XRD, MiniFlex II), Thermogravimetry and Differential Scanning Calorimetry (TG-DSC) and Field Emission Scanning Electron Microscope (FE-SEM, MIRA II LMH).

3. Results and Discussion

Solvothermal processing conditions such as pH, reaction temperature and solvent ratio, have significant effects on the formation, phase component, morphology and particle size of yttria powders. Ethylene glycol is a versatile widely used, cheap, and safe capping organic molecules for uniform nanoparticles except as a solvent.³¹⁻³³⁾ Fig. 2 shows the XRD patterns of the synthesized powders obtained reaction at 250°C for 6h. The detectable diffraction peaks in the pattern can be well indexed to the yttrium hydroxide (JCPDS card no. 09-0062) and yttrium oxide hydroxide nitrate (JCPDS card no. 79-1352). Fig. 3 shows the XRD pattern of the synthesized yttria powders after heat treatment at 600°C for 2h. The detectable four strong and broad peaks at $2\theta \approx 29.2, 33.8, 48.5$ and 57.6° are present in the XRD pattern, which can be assigned to (222), (400), (440) and (622) reflections of cubic Y_2O_3 .

Fig. 1. Experimental flow chart of synthesized yttria powders by a modified solvothermal process.

Fig. 2. X-ray diffraction pattern of yttria powders synthesized reaction at 250°C for 6h as a function of solvent (water/ethylene glycol) ratio ; (a) 1:9, (b) 1:1 and (c) 9:1.

Fig. 3. X-ray diffraction pattern of yttria powders synthesized by a modified solvothermal processing with heat treatment at 600°C for 2h as a function of solvent (water/ethylene glycol) ratio ; (a) 1:9, (b) 1:1 and (c) 9:1.

Fig. 4. TG-DSC curves of synthesized Y_2O_3 powders reaction at 250°C for 6h.

respectively (JCPDS card no. 89-5591). However, the phase of the synthesized powder was mixed $Y(OH)_3$ and Y_2O_3 with water to ethylene glycol ratio is 1 to 9.

Fig. 5. The schematic illustration of the formation mechanism of Y_2O_3 in ethylene glycol at mild temperature and pressure condition.

Fig. 4 shows the TG-DSC curves of the synthesized Y_2O_3 powders reaction at 250°C for 6h. The TG-DSC curves showed two step weight loss of ca. 22% with two endothermic peaks at about 380°C and 485°C which may be due to combustion of residual organics.

The schematic illustration of the formation mechanism of Y_2O_3 in ethylene glycol at mild temperature and pressure condition.³⁴⁾ In this case, when the concentration of ethylene glycol is low, only certain facets of the nuclei are attached with ethylene glycol ions and lead to an anisotropic growth of the Y_2O_3 and hexagonal are obtained. Increasing the concentration of ethylene glycol, all the facets of the nuclei are absorbed with ethylene glycol ions and the growth rates in all directions are similar, and thus microspheres are obtained.

The samples were observed under SEM, and the corresponding images are shown in Fig 5. The morphology of the obtained Y_2O_3 powders was characterized by scanning electron microscope (SEM) observations. As shown in Fig. 5, the average crystalline sizes and morphology of the synthesized Y_2O_3 particles changed with water to ethylene glycol ratio. The average size and shape of the synthesized powders was 0.5-1 μm and spherical reaction at 250°C for 6h in water to ethylene glycol ratio 1 to 9. The morphology of the synthesized powders are almost hexagonal with diameters about 0.5~1 μm and length about 2 μm after the reaction at 250°C for 6h in water to ethylene glycol ratio 9 to 1.

Fig. 6. SEM images of yttria powders synthesized reaction at 250°C for 6h after heat treatment at 600°C for 2h as a function of solvent (water/ethylene glycol) ratio ; (a) 1:9, (b) 1:1 and (c) 9:1.

4. Conclusion

Yttria powders were synthesized by a modified solvothermal processing reaction at 250°C for 6h. The crystal structure and morphology were characterized by XRD, TG-DSC and FE-SEM. The detectable four strong and broad peaks at $2\theta \approx 29.2$, 33.8, 48.5 and 57.6° are present in the XRD pattern, which can be assigned to (222), (400), (440) and (622) reflections of cubic Y₂O₃ respectively (JCPDS card no. 89-5591). However, the phase of the synthesized powder was mixed Y(OH)₃ and Y₂O₃ with water to ethylene glycol ratio is 1 to 9. The average crystalline sizes and morphology of the synthesized Y₂O₃ particles changed with water to ethylene glycol ratio. The average size and shape of the synthesized powders was 0.5-1 μm and spherical after the reaction at 250°C for 6h in water to ethylene glycol ratio 1 to 9. The average particle size and distribution of the synthesized yttria powders were in the range of 0.5~2 μm and broad, respectively. In this study, the distilled water and ethylene glycol play critical roles in the formation of the Y₂O₃ particles.

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