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Synthesis of Nanosized CeO_2 Powders by Hydrothermal Process

Dong-Sik Bae† and Yeong-Kyeun Paek*

Division of Ceramics, Korea Institute of Science & Technology, Seoul 136-791, Korea
**Department of Materials Science & Engineering, Andong National University, Andong 760-749, Korea*
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ABSTRACT

Nanosized CeO_2 powders were prepared under high temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. Spherical shape of CeO_2 powder was obtained at 175°C for 6 h. TEM and X-ray diffraction patterns showed that the synthesized particle was crystalline. The average size and size distribution of the synthesized particles were below 30 nm and narrow, respectively. In addition, the effects of synthesis parameters under hydrothermal process are discussed.

Key words : CeO_2, Nanosized powder, Hydrothermal process, Spherical shape

Recently, there has been an increasing interest in the synthesis of the cerium oxide because it is used as an oxygen conductor in Solid Oxide Fuel Cells (SOFC), electrolyzers, oxygen pumps, and amperometric oxygen monitors. The cerium oxide is also useful as one of the highly refractory oxides.[1] The cerium oxide, however, is difficult to be sintered to high density without sintering additives.[2]

Hydrothermal processes have the 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.[3] This process can produce fine, high-purity, and stoichiometric particles of single and multi-component metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, the desired shape and size of the particles can be produced.[4,5] Uniform distribution of the particles is a key to maintaining high reliability for optimal control of grain size and microstructure. These powders could be sintered at low temperature without calcination and milling steps.[6,7] In this study, nanosized CeO_2 crystalline particles were obtained by a hydrothermal process.

For experiment, chemicals were used as the received from Aldrich Chemical Co. Deionized water was used for all experiments. The process for preparing cerium oxide powders by hydrothermal process in aqueous solution is schematically illustrated in Fig. 1. Cerium oxide precursor was precipitated from 1 M $Ce(NO_3)_3 \cdot 6H_2O$ solution by slowly adding 1 M KOH solution with rapid stirring. The solutions were placed in a 1000 ml stainless steel pressure vessel and heated to reaction temperature at the rate of 10°C/min. The pressure of the reactor gradually increased to about 129 psi and kept around 129 psi during the reaction at 175°C. The reaction products were washed five times by repeated cycles of centrifugation and re-dispersion in deionized water. The recovered powders were analyzed for phase composition using X-ray diffraction (Phillips, PW 1825/00) over the 2 theta range from 10-80 at the rate of 5.0°/min. The morphology of the synthesized particles was observed using scanning electron microscopy (SEM, Hitachi S-4200) and transmission electron microscopy (TEM, Philips, JEM-200CX).

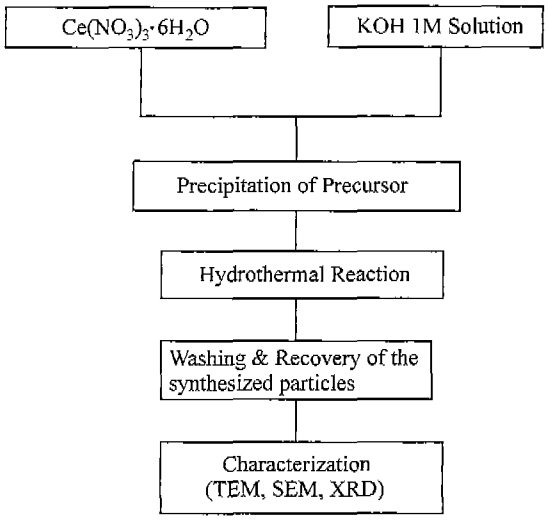

Fig. 1. Experimental flow chart of synthesis of the cerium oxide particles by hydrothermal reaction.

The hydrothermal conditions have significant effects on the formation, phase component, morphology and particle size of CeO_2 products. The pH in the reaction medium affected significantly the formation of CeO_2 products. The precipitation of the $Ce(NO_3)_3 \cdot 6H_2O$ was prepared with 1 M

†Corresponding author : dsbae@kist.re.kr

KOH solution as a function of pH of starting solutions. Among the starting solutions, the pH of starting solution was 10.18. The reaction temperature had a great effect on the grain size of the products and the agglomeration among grains. Lowering temperature gives rise to decreasing grain size and increasing agglomeration among grains.[8] It has been proposed that crystallization under hydrothermal conditions proceeds by dissolution-precipitation and structural

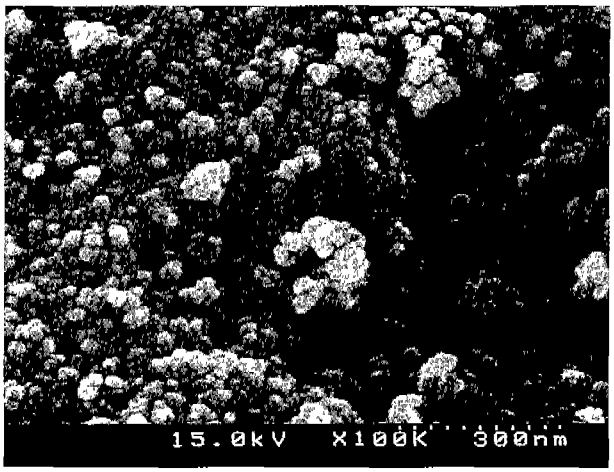

Fig. 2. SEM micrograph of the synthesized particles by hydrothermal reaction at 175°C for 6 h.

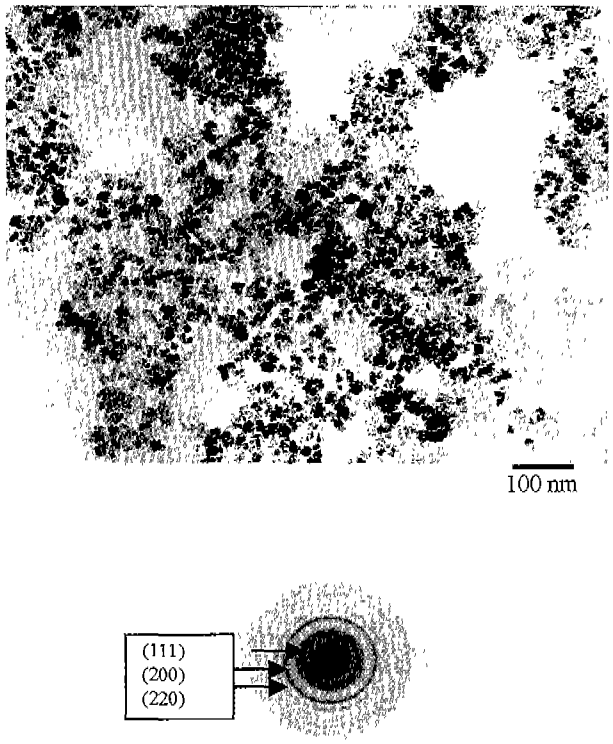

Fig. 3. TEM micrographs and diffraction pattern of the synthesized particles by hydrothermal reaction at 175°C for 6 h.

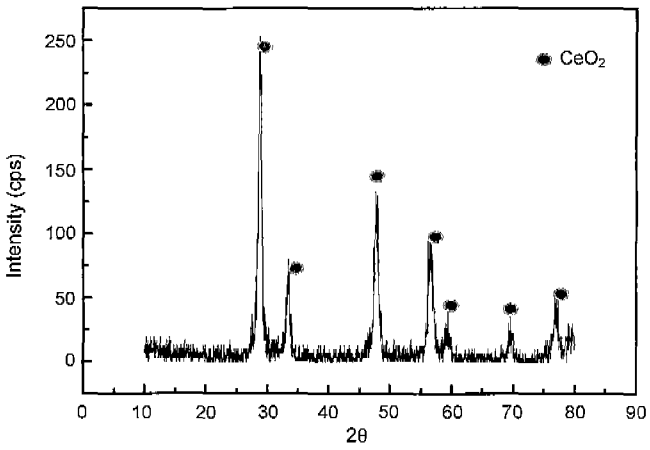

Fig. 4. X-ray diffraction patterns of the synthesized particles by hydrothermal reaction at 175°C for 6 h.

rearrangement.[9] The reaction time plays an important role in the phase transformation from cerium hydroxide to cerium oxide. In this study, the reaction temperature was 175°C and reaction time was 6 h.

Fig. 2 and Fig. 3 show the scanning electron microscopy and transmission electron microscopy of the synthesized particles, respectively. From the TEM diffraction pattern in Fig. 3, the synthesized particles were known as a polycrystalline phase of CeO_2. The average size and size distribution of the synthesized particles were below 30 nm and uniform, respectively. The shape of the synthesized particles was nearly spherical type. Fig. 4 shows the X-ray diffraction pattern of the synthesized particles in aqueous solution. From the X-ray analysis, the crystalline phase of the synthesized particles was CeO_2. The result supports therefore that of the ring diffraction pattern from the polycrystalline phase in Fig. 3.

In conclusion, the nanosized CeO_2 particles were prepared under high temperature and pressure conditions by precipitation from $Ce(NO_3)_3 \cdot 6H_2O$ with aqueous potassium hydroxide. Spherical shape of CeO_2 powder was obtained at 175°C for 6 h. From the TEM and X-ray analysis, the synthesized particle was crystalline. The average size and size distribution of the synthesized particles were below 30 nm and narrow, respectively. The results of this study show that the synthesis of the nanosized CeO_2 particles with crystalline phase is possible under hydrothermal condition in aqueous solution.

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