

The hydrothermal synthesis of ultrafine cerium(IV) oxide powders

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Hydrothermal synthesis is an attractive method for the preparation of crystalline ceramic oxide powders and has been employed for the synthesis of fine powders [1]. CeO_2 is one of the highly refractory oxides and is difficult to sinter to a high density without sintering aids, therefore CeO_2 needs to be produced as a fine powder for good sinterability. Up to now, few attempts have been made for the preparation of fine CeO_2 particles. Matijevic and Hsu [2] showed that the crystalline compound of a hydroxyl carbonate compound ($\text{Ce}_2\text{O}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$) with a spherical shape was precipitated in a urea solution and the compound was converted to cubic CeO_2 with calcination at 400°C . Chu *et al.* [3] studied the sintering of the cerium-containing particles obtained from urea solutions. Chen and Chen [4] reported the preparation of fine CeO_2 powders using the homogeneous precipitation method and a hexamethylenetetramine (HMT). In accordance with the hydrothermal synthesis, Tani *et al.* [5] studied the effect of mineralizers on the crystallization of CeO_2 under hydrothermal conditions at $500\text{--}600^\circ\text{C}$ and 100 MPa. Zhou and Rahaman [6] investigated the sintering of ultrafine hydrothermally synthesized CeO_2 powders. However, the factors affecting the hydrothermal process have not been clarified.

In the present study, ultrafine CeO_2 powders were synthesized in the presence of an excess amount of ammonia in an autoclave at $150\text{--}200^\circ\text{C}$. The effects of treatment temperature, treatment time and the concentration of the starting solution on the crystal growth of CeO_2 under hydrothermal conditions were investigated.

The solutions of cerium(IV) sulphate tetrahydrate, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, were stirred well and an excess amount of ammonia solution was added. The resulting precipitate, which was prepared in 20 ml Teflon bottles without separating the precipitate from its mother liquor, was sealed with a cap and placed in a stainless steel laboratory autoclave vessel, which was heat treated for a specific time at $150\text{--}200^\circ\text{C}$. The products prepared by the hydrothermal treatment were washed with distilled water, dried in air and characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The crystallite sizes of the phases were calculated from the Scherrer formula using the (220) diffraction peak of CeO_2 .

The results of the experiment on the effect of treatment temperature on the hydrothermal products are shown in Fig. 1. The XRD patterns show all of the major reflections of CeO_2 with a fluorite structure with no sign of an amorphous form. It

is obvious that the higher the hydrothermal treatment temperature, the sharper the characteristic peaks of CeO_2 . The evolution of the crystallite sizes was investigated during the hydrothermal treatment. The particle size of the powder synthesized at 150°C for 20 h was 3 nm, which confirms the original Scherrer X-ray line-broadening estimate.

Fig. 2 summarizes the data obtained from the line-broadening analysis of the (220) XRD peak

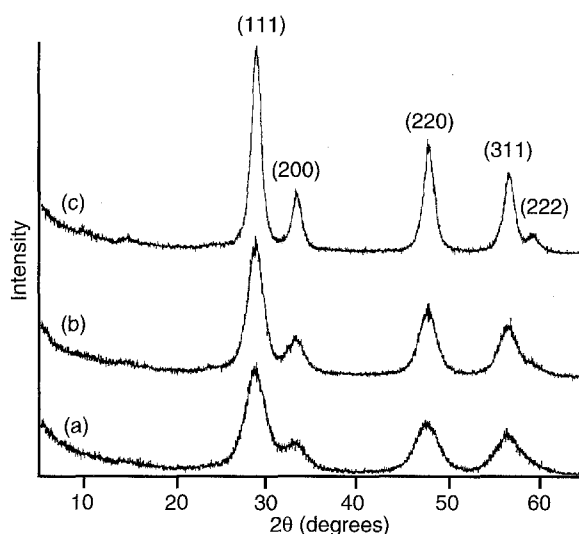


Figure 1 XRD patterns for powders prepared from 0.1 mol l^{-1} solutions under hydrothermal conditions at (a) 150°C for 20 h, (b) 180°C for 20 h and (c) 200°C for 20 h.

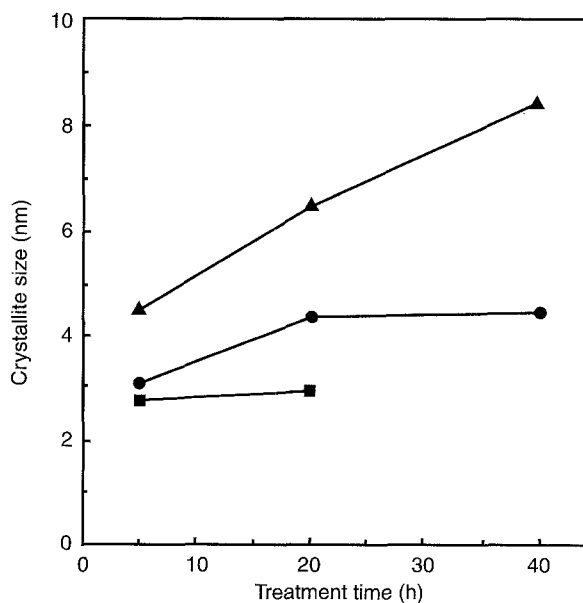


Figure 2 Crystallite size for powders prepared from 0.1 mol l^{-1} solutions at (■) 150°C , (●) 180°C and (▲) 200°C plotted against the hydrothermal treatment time.

as a function of treatment time. As can be seen, the crystallite size grows slowly with the hydrothermal treatment time. The crystallite size for the hydrothermal treatment at 200 °C for 5 h was 4.5 nm. However, the hydrothermal treatment at 200 °C for

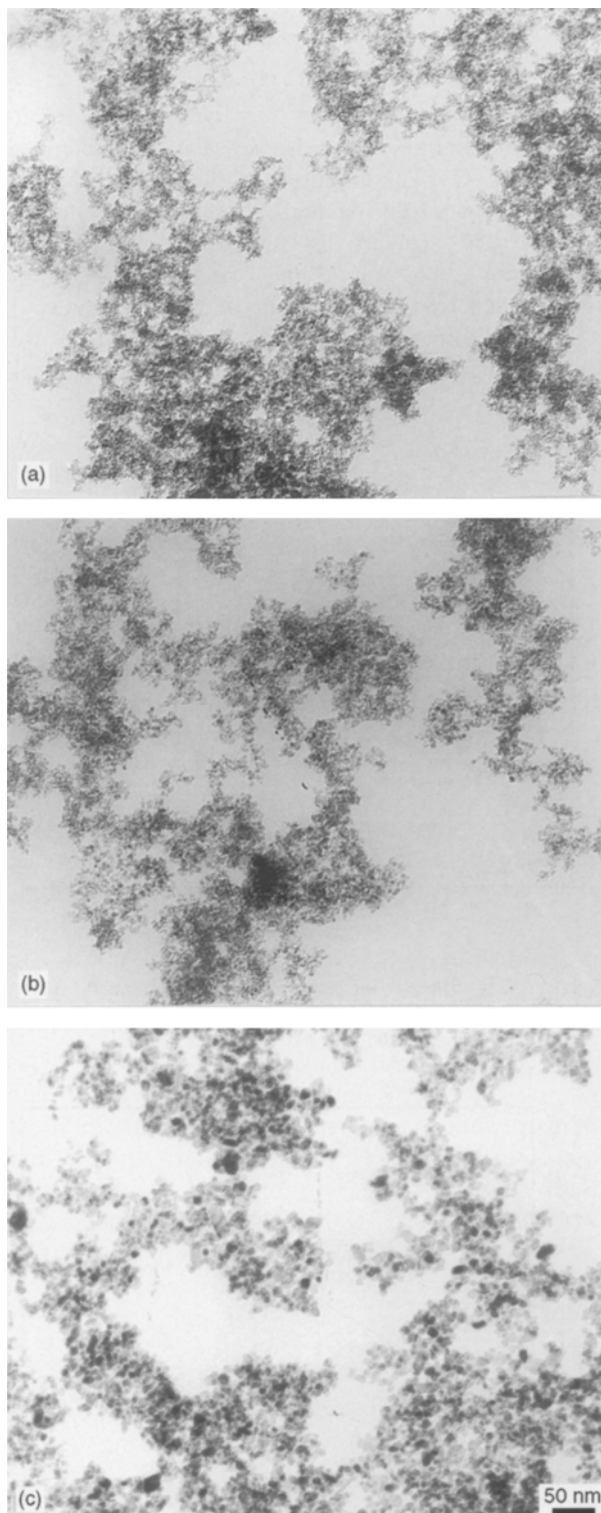


Figure 3 TEM photographs of powders prepared from 0.1 mol l⁻¹ solutions under hydrothermal conditions at (a) 150 °C for 5 h, (b) 180 °C for 40 h and (c) 200 °C for 40 h.

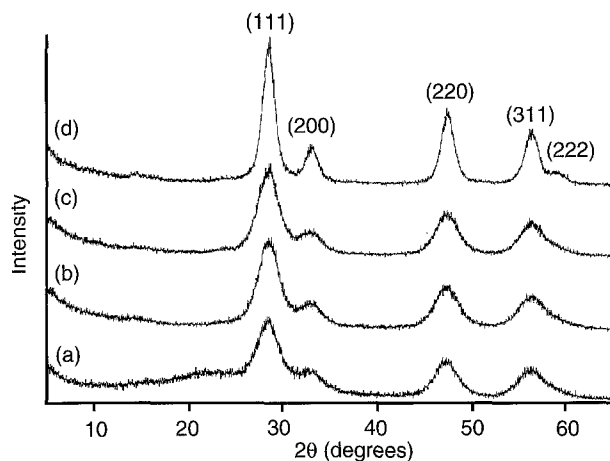


Figure 4 XRD patterns for powders prepared from (a) 0.01 mol l⁻¹, (b) 0.1 mol l⁻¹, (c) 0.5 mol l⁻¹ and (d) 1.0 mol l⁻¹ solutions under hydrothermal conditions at 180 °C for 5 h.

40 h increased the crystallite size by about twofold to 8.5 nm. Fig. 3 shows the morphology of the synthesized ceria powders. For the TEM examination, the slurry was heavily diluted with ethyl alcohol, partially deagglomerated by ultrasonics, and directly run over a collodion film on the copper TEM grid. The TEM photographs also showed that the powders obtained from the cerium(IV) sulphate tetrahydrate under hydrothermal conditions were very fine, much finer than the powders from the Ce-HMT method by Chen and Chen [4].

The XRD profiles of the powders synthesized from various concentrations of cerium(IV) sulphate solutions are shown in Fig. 4. The crystallinity and crystallite size of the synthesized powders depend on the concentration of the solution. As the cerium sulphate in the starting solution was concentrated, the CeO₂ peaks became sharper. From these results, the conditions for synthesizing ultrafine CeO₂ powders under hydrothermal conditions have been clarified.

References

1. W. J. DAWSON, *Ceram. Bull.* **67** (1988) 1673.
2. E. MATIJEVIC and W. P. HSU, *J. Colloid Interf. Sci.* **118** (1987) 506.
3. X. CHU, W. CHUNG and L. D. SCHMIDT, *J. Amer. Ceram. Soc.* **76** (1993) 2115.
4. P. L. CHEN and I. W. CHEN, *ibid.* **76** (1993) 1577.
5. E. TANI, M. YOSHIMURA and S. SOMIYA, *J. Mater. Sci. Lett.* **1** (1982) 461.
6. Y. C. ZHOU and M. N. RAHAMAN, *J. Mater. Res.* **8** (1993) 1680.

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