

# Nanostructured Cerium Oxide: Preparation and Properties of Weakly-agglomerated Powders

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## Abstract

*Nanocrystalline powders of cerium oxide were prepared from cerium(III) nitrate solution by a two-stage precipitation process which yielded weakly-agglomerated powders with a crystallite size smaller than 5 nm. Hydrogen peroxide was added to cerium nitrate at 5°C to slowly oxidise  $Ce^{3+}$  to  $Ce^{4+}$  and thereby initiate homogeneous precipitation with the formation of dense spherical agglomerates. The precipitation process was completed by the addition of ammonium hydroxide which disrupted the spherical agglomerates leaving a weakly-agglomerated powder of hydrated ceria. The process was completed by hydrothermal treatment at 180°C without increase in crystallite size. The powders were characterised by X-ray diffraction, transmission electron microscopy and thermogravimetric analysis. The weakly-agglomerated state of the powder and the uniform crystallite size of under 5 nm are favourable characteristics for many applications. © 1999 Elsevier Science Limited. All rights reserved*

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## 1 Introduction

The increased performance demanded of advanced ceramic materials imposes increasingly stricter requirements on the ceramic powders from which they are made. The use of monodisperse nanocrystalline powders as starting materials has demonstrated considerable potential for improving the properties of existing ceramic compositions. Cerium oxide,  $CeO_2$ , is an example of a material where the number of applications has increased rapidly, e.g. glasses, ceramics, phosphors, catalysis, and chemical

applications, and for which the use of nanocrystalline powders is an important factor. Unfortunately, the high specific surface areas of nanocrystalline powders, in which the primary particle size is often smaller than 5 nm, also results in a stronger tendency of the powder to agglomerate which can make processing difficult. Weakly-agglomerated powder is needed both for dry processing methods, e.g. powder compaction, and for the preparation of stable suspensions in liquids, e.g. for thin or thick film production. Unless weakly-agglomerated nanoscale powders can be produced, the benefits expected from highly-uniform nanocrystalline powders are easily lost during the manufacture of components. The strength of agglomerates depends on the surface properties of the nanocrystalline particles in the powder and these properties are sensitively dependent on the powder synthesis procedures. In this paper we compare ceria powders derived from precursors prepared by precipitation with hydrogen peroxide with those of precursors prepared by conventional precipitation with ammonia. We conclude that powders precipitated with hydrogen peroxide are significantly more weakly agglomerated as well as having a smaller crystallite size, i.e. less than 5 nm.

The large scale production of powders needs to be economically feasible and the methods used for nanostructured powders for advanced applications should not be more complex than those of conventional processes. Precipitation from aqueous solution is widely used in industry for producing ceramic oxide powders, but for nanocrystalline materials, such powders tend to form excessively hard agglomerates. The precipitated species is usually a precursor, e.g. a hydroxide, rather than the required oxide and a thermal decomposition treatment is needed to obtain the final product. In densely agglomerated nanostructured powders there are many points of contact between primary particles and even a low-temperature thermal decomposition treatment allows sufficient diffusion

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to occur to produce agglomerates too hard to be easily redispersed. Dense agglomerates must therefore be avoided during the precipitation process if easily processable powders are to be obtained. Control of agglomerate morphology requires control of the chemistry of the precipitation reaction.

Precipitation occurs by adding a precipitating ligand (anion) to a solution containing the metal cation. If the precipitating ligand is added directly by simply pouring one solution into another then there is little control of the chemistry during precipitation because of the large and inhomogeneous gradients in solution concentration. A better control of chemical and morphological characteristics can be achieved if the precipitating ligands are generated 'in situ' simultaneously and uniformly throughout the solution, i.e. a homogeneous precipitation process. An example of the homogeneous precipitation is to increase the pH of the solution by the thermal decomposition of urea or hexamethylenetetramine to form ammonia and thereby to generate  $\text{OH}^-$  as the precipitating ligand.<sup>1</sup> Monodispersity of the precipitated particles results from the occurrence of nucleation in a single burst followed by a uniform growth process, e.g. according to the LaMer theory. The primary particles resulting from such a nucleation process are usually monodisperse and several nanometers in size. Amorphous precipitates such as aluminium hydroxide usually consist of spherical particles whereas crystalline precipitates often consist of faceted particles. Ageing of such a solution usually leads to agglomeration of the primary particles to form densely packed agglomerates. The agglomerates often have a fairly narrow size distribution and tend to be spherical in the case of amorphous precipitates where there is no ordering force such as a dipole moment or a difference in the surface energy between the crystal facets of the primary particles. Agglomerate diameters up to 1 micron are frequently obtained.

The homogeneous precipitation process based on forced hydrolysis is quite widely applicable and has been used to produce various monodisperse metal oxide precursor particles of various shapes and sizes.<sup>1</sup> Forced hydrolysis is usually accomplished either by increasing the pH of the solution, or by heating the solution, in some cases at temperatures up to boiling point at atmospheric pressure, but more usually to higher temperatures under pressure (i.e. hydrothermal treatment).

There are several reports of methods for the preparation of ceria that depend on an increase in pH to cause precipitation. Matijevic and Hsu<sup>2</sup> obtained non-spherical crystalline particles of  $\text{CeO}(\text{CO}_3)_2\text{H}_2\text{O}$  by precipitation with urea. Aiken *et al.*<sup>3</sup> used the same method to obtain spherical

particles of a mixed Y(III)/Ce(III) compound. Akinc and Sordelet<sup>4</sup> prepared non-spherical well-crystallised  $\text{CeOHCO}_3$  particles. Chen and Chen<sup>5</sup> used hexamethylenetetramine decomposition to prepare cerium oxide powders and compared them with those precipitated with ammonium hydroxide.

Heating the solution to force hydrolysis has been reported by several authors. Briois *et al.*<sup>6</sup> reported the preparation of 3 nm particles of  $\text{CeOSO}_4\cdot\text{H}_2\text{O}$  from Ce(IV) sulphate at 900°C, but this is not an attractive precursor for ceria due to the presence of the sulphate group. Hydrothermal conditions appear more suitable for the direct preparation of ceria. Hirano and Kato<sup>7</sup> obtained fine cerium oxide from Ce(III) nitrate, Ce(IV) sulphate and Ce(IV) ammonium sulphate solutions at 180°C under autogenous pressure. Stable suspensions of well-crystallised cerium and cerium oxide doped with 6 at% Y were hydrothermally synthesised at temperatures up to 300°C by Yang and Rahaman.<sup>8</sup>

The homogeneous precipitation results cited above, which all depend on forced hydrolysis to cause precipitation, succeed in controlling agglomerate morphology and yield agglomerates with a narrow size distribution. However, in the case of precipitation by increase of pH, the agglomerates were densely packed and because the primary particles tend to be strongly bound together by surface forces, the resulting agglomerates are not easily redispersed. Hydrothermal treatments were generally more successful in producing weakly agglomerated powders, but the crystallite size tended to be considerably larger. These results demonstrate that powder characteristics are sensitively dependent on the method of preparation so that, in principle, there is considerable scope to try to engineer the powder properties to suit a particular application. Uniformly-sized crystallites smaller than 5 nm, or loosely-bound agglomerates have been produced with the methods mentioned above, but obtaining both characteristics in one powder with them appears difficult to achieve. Forced hydrolysis by increase of pH or of temperature is the common factor in these methods, and if it is this that restricts the range of powder properties that can be achieved, then alternative precipitation chemistries might offer a better route to weakly-agglomerated nanoscale powders.

Several other chemical techniques have been used to prepare nanocrystalline ceria. For example, Brittain and Gradoff<sup>9</sup> prepared stable colloidal dispersions of cerium oxide in inert organic media using organic acids. Woodhead<sup>10</sup> reported another chemical approach for colloidal cerium oxide which is of interest because cerium(IV) hydroxide was precipitated from Ce(III) nitrate using a mixture of ammonium hydroxide and hydrogen peroxide in

which the role of the  $\text{H}_2\text{O}_2$  was to convert Ce(III) to the more easily hydrolysed Ce(IV). This was a non-homogeneous precipitation process, but the concept of precipitation by hydrolysis due to a change in oxidation state, rather than due to a change in pH or temperature, appears to be a synthesis route worth additional investigation.

The approach that we have used to produce weakly-agglomerated powders can be regarded as a homogeneous precipitation variation on the method of Woodhead,<sup>10</sup> with the difference that precipitation was by a two step process which yielded  $\text{Ce}(\text{OH})_3\text{OOH}$  instead of  $\text{Ce}(\text{OH})_4$ . Cerium has two oxidation states, Ce(III) and Ce(IV), with different degrees of hydrolysability in aqueous solution, and the oxidation of the Ce(III) to Ce(IV) can be achieved using hydrogen peroxide alone. Simply adding  $\text{H}_2\text{O}_2$  to Ce(III) nitrate solution at room temperature causes immediate reaction in an inhomogeneous manner but homogeneous precipitation can be easily achieved in this system by first cooling the reactants to about  $5^\circ\text{C}$  before mixing. At  $5^\circ\text{C}$  the reaction kinetics are slow enough to enable the reactants to be mixed before precipitation can occur. Homogeneous precipitation occurred on allowing the solution to stand for about 10 min, or on warming, and precipitation was therefore induced by a change in oxidation state of the cation and not by an increase in pH. Not all Ce was precipitated from solution by this method and it was found necessary to add ammonium hydroxide to complete the reaction, the product of which is believed to be  $\text{Ce}(\text{OH})_3\text{OOH}$  and not the  $\text{Ce}(\text{OH})_4$  which is otherwise obtained when ammonium hydroxide alone is used as the precipitating agent.

Ce(III) nitrate was used as the starting material because of the relatively easy decomposition of the nitrate anion on calcination and because nitric acid is often used as a peptising agent if colloidal sol is prepared from the powder. The precipitate was hydrothermally treated to form the oxide which consisted of nanoscale crystallites weakly bonded within agglomerates. The solid oxide precursors and cerium oxide were characterised using differential thermal analysis (DTA), thermogravimetric analysis (TG), X-ray diffraction (XRD) and transmission electron microscope (TEM) techniques.

## 2 Experimental Procedure

### 2.1 Starting materials

The starting materials used were: cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , anal., Alfa-Johnson Matthey), hydrogen peroxide (30%  $\text{H}_2\text{O}_2$ , p.a., Merck) and ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 25 vol% p.a., Merck).

### 2.2 Synthesis of the solid oxide precursor, hydrothermal treatment and calcination

Three synthesis routes, referred to as methods A, B and C, were used for preparation of cerium oxide powder as described below.

- *Method A:* Ammonium hydroxide was added dropwise to a stirred solution of  $0.1 \text{ mol l}^{-1}$  Ce(III)-nitrate in water until a solution pH of 10 was reached. The white or yellowish gel-like precipitate that formed settled rapidly. A sample of the gel-like initial precipitate was prepared for analysis by removing the supernatant and washing the precipitate twice with a double volume of distilled water and then drying at  $80\text{--}85^\circ\text{C}$  overnight. The remainder of the product was hydrothermally treated at  $18^\circ\text{C}$  for 4 h under autogenous pressure without stirring to obtain cerium oxide. After cooling, the clear supernatant was decanted and the yellowish precipitate was washed with about 200 ml distilled water and then dried at  $80\text{--}85^\circ\text{C}$  overnight.
- *Method B:* A solution of  $0.1 \text{ mol l}^{-1}$  Ce(III) nitrate in water was mixed with 30 vol% hydrogen peroxide in a volume ratio of 3:1 at various temperatures: at about  $5^\circ\text{C}$ , at room temperature, and a solution which was mixed at RT was heated to boiling temperature. An orange-yellow transparent sol appeared in all cases: after 8–10 min at  $5^\circ\text{C}$  and after 2–3 min at RT, or on heating to boiling point. The sol produced at  $5^\circ\text{C}$  and aged at that temperature for 12 h was stable at room temperature for more than one week without any settling of the solid phase. In contrast, sol produced at room temperature and by heating to boiling partially sedimented. The precipitated sol particles were separated by centrifugation for further examination.
- *Method C:* Separate solutions of  $0.1 \text{ mol l}^{-1}$  Ce(III) nitrate in water and of 30 vol% hydrogen peroxide were cooled to  $5^\circ\text{C}$  and then mixed together under constant stirring. After 8–10 min the solution turned first yellow then orange-yellow, but remained transparent. Ammonium hydroxide solution was then added to increase the pH value to 10. Above a pH of 9–9.2 the pH increased only slowly in response to further addition of ammonium hydroxide solution and an orange precipitate settled rapidly from solution. Precipitation therefore occurred in two stages. The solution was decanted and the precipitate was washed and dried at  $80\text{--}85^\circ\text{C}$  or hydrothermally treated as described under method A above.

Samples of powders synthesised by methods A, B and C were calcined in air to 300 and 500°C in alumina crucibles at a heating rate 2°C min<sup>-1</sup> with a dwell time of 1 h at temperature.

### 2.3 Analysis

The precipitated ceria precursor and calcined products were characterised using several techniques to determine particle size, composition and morphology. Differential thermal analysis and thermogravimetric analysis (DTA/TG, Netsch STA 409) was made in a dry-air atmosphere using a heating rate of 2°C min<sup>-1</sup>. Samples for transmission electron microscopy (TEM, Philips EM 400) of the precipitated ceria precursor were prepared by dipping carbon-coated copper grids into a dilute water suspension of the particles immediately after synthesis. The grids were then dried at room temperature or at 80–85°C. The calcined product was dispersed in absolute ethyl alcohol by ultrasonification (3–5 min) and a drop of a suspension was allowed to evaporate on the grid at room temperature. X-ray diffraction analysis (XRD, Philips PW173) was used to determine phase composition and to estimate the crystallite size of the powders. A 2θ range of 5–80° was used and the apparent crystallite size was estimated from peak broadening using the Scherrer equation:  $D_{\text{app}} = K\lambda / (B \cos \theta)$ , where  $K = 0.9$  and  $B =$  peak width obtained using a Voigt peak fitting routine.  $\text{CuK}\alpha$  radiation with a graphite filter was used ( $\lambda = 1.5406$ ) and the instrumental broadening was determined using an  $\text{LaB}_6$  standard.

## 3 Results

### 3.1 Precipitation of the ceria precursor

The precipitates produced by the three different methods differed significantly, primarily due to the presence of different anion species (–OH, –OOH, or –OH + –OOH) and to the reaction temperature used. The use of ammonium hydroxide alone (method A) resulted in a voluminous white or yellowish gel-like precipitate from Ce(III) nitrate solution. In principle the precipitate should be  $\text{Ce}(\text{OH})_3$ , which is white and is a definite compound rather than a hydrous oxide. Oxidation of  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  in solution has been suggested<sup>5</sup> at high pH, i.e.  $\text{Ce}^{3+} + \text{H}_2\text{O} \rightarrow \text{Ce}(\text{OH})^{3+} + \text{H}^+ + \text{e}^-$  with subsequent hydrolysis to  $\text{Ce}(\text{OH})_4$  and precipitation. However, oxidation of  $\text{Ce}(\text{OH})_3$  also occurs readily in air at room temperature to form yellow  $\text{Ce}(\text{OH})_4$ .  $\text{Ce}(\text{OH})_4$  is a hydrous oxide which can also be described as  $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  which dehydrates progressively, i.e.  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$  where  $n \leq 2$ . The product of precipitation with ammonium

hydroxide is therefore likely to be  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$  rather than  $\text{Ce}(\text{OH})_3$ . Precipitation from Ce(III) nitrate using hydrogen peroxide alone (method B) resulted in a fine sol which formed faster at boiling temperature than at 5°C or at room temperature. The stability of the sol solution, as defined by the first appearance of settled solid, was several days for sol produced at 5°C, and several minutes for sol produced at boiling temperature. Hydrogen peroxide alone was not capable of precipitating all cerium ions from solution. Complete precipitation of cerium ions was achieved using hydrogen peroxide + ammonium hydroxide (method C). The orange-yellow precipitate was formed by a two step process, first the initiation of hydrolysis and complexation with hydrogen peroxide followed by quantitative precipitation with ammonium hydroxide to pH of about 10. The precipitate settled rapidly and it was easily separated from solution. The precipitates were stable in water but the dry precipitate slowly transformed to crystalline cerium oxide in air at room temperature.

### 3.2 X-ray diffraction measurements

X-ray diffraction spectra identified all the powders as cerium oxide. The peaks in the spectra of powders precipitated by ammonia alone were narrow and well-defined with a good signal-to-noise ratio; those of the other powders were all much broader and less intense. We attributed peak broadening to small crystallite size and calculated apparent crystallite sizes as shown in Table 1. The ceria powder derived from the –OH (method A) and –OOH + –OH (method C) precipitates by hydrothermal treatment were both weakly agglomerated, but the powder from mixed ligand precipitate had a significantly smaller apparent crystallite size (4.2 nm compared with 26.8 nm).

### 3.3 Thermal analysis (TG/DTA)

Information about the chemical composition of the precipitates was deduced from the thermogravimetric weight loss measurements by comparing measured values with the theoretical weight losses for plausible decomposition reactions, e.g. the

**Table 1.** Crystallite size of ceria powders calculated from XRD peak broadening (Scherrer equation)

Sample preparation parameters			Crystallite size (nm) after thermal treatment		
Method	Temperature	Autoclaved	12 h at 80–85°C	1 h at 300°C	1 h at 500°C
A	RT	No	15.4	15	27
A	RT	Yes	26.8	27	26
B	100°C	No	3.2	4.4	—
C	50°C	No	3.4	5.2	13
C	RT	Yes	4.2	4.5	10

decomposition of hydrated oxide, i.e.  $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CeO}_2$  should result in a weight loss of 17.29%. The XRD spectra indicated that  $\text{CeO}_2$  was present in all samples, but the additional presence of amorphous  $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot n\text{H}_2\text{O}$  could be not excluded.

The precipitate obtained by method A (the addition of ammonium hydroxide alone) after drying overnight at 80–85°C showed a weight loss of 6.2% and a weight loss of 3.1% after hydrothermal treatment, as shown in Fig. 1. These weight losses are lower than those corresponding to the decomposition of  $\text{Ce}(\text{OH})_3$  (9.95%) or  $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  (17.3%) and indicate that the samples consisted either of a partially hydrated form of ceria, i.e.  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ , for which a 6.2% weight loss on decomposition corresponds to  $n=0.59$ , or that it consisted of a mixture of phases e.g.  $\text{CeO}_2 + \text{CeO}_2 \cdot 2\text{H}_2\text{O}$ . A weak exothermic peak at about 280°C, which might correspond to the crystallisation of anhydrous ceria, was clearly present in Fig. 1(A), but was scarcely evident in Fig. 1(B) for the hydrothermally treated sample.

The precipitate obtained by method B (precipitation with hydrogen peroxide alone) showed a total weight loss of 16.8% for the precipitation procedure carried out at boiling point as shown in Fig. 2. This total weight loss corresponds well with that expected for  $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  decomposition (17.3%). The decomposition appeared to occur in three distinct stages and was not complete until >800°C, but the DTA curve did not show the exothermic peak at 280°C that was observed in Fig. 1(A).

The precipitate obtained by method C (precipitation with hydrogen peroxide followed by ammonium hydroxide) at 5°C showed a total weight loss of 23.0% as shown in Fig. 3 which corresponds closely to that expected for the decomposition of  $\text{Ce}(\text{OH})_3\text{OOH}$  (23.2%) assuming that a single phase was initially present. The DTA curve in Fig. 3(A) showed two well-defined events. The first event produced an endothermic peak at about

80°C, which might be due to dehydration, or it might correspond to the transformation:  $\text{Ce}(\text{OH})_3\text{OOH} \rightarrow \text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ , with a theoretical weight loss of 7.1%. The second event generated a well-defined exothermic peak at 250–280°C which might correspond to the crystallisation of  $\text{CeO}_2$  occurring at a slightly lower temperature than in the case of that obtained with method A [see Fig. 1(A)]. After ageing freshly-prepared precipitate for 4 h at 100°C the TG weight loss was 15.1% which does not correspond to the decomposition of any single compound and would be consistent with the presence of a mixture of species due to the complete decomposition of the initial phase e.g. of  $\text{Ce}(\text{OH})_3\text{OOH}$  to  $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  and the partial decomposition of  $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CeO}_2 \cdot n\text{H}_2\text{O}$  where  $n < 2$ . The DTA curve was consistent with the interpretation of the TG curve given above i.e. it no longer showed an endothermic peak at 80°C and the exothermic peak at 250–280° was still present but was slightly less intense compared with that for the precipitate prepared at 5°C.

### 3.4 Transmission Electron Microscopy (TEM)

TEM analysis provided information on the size and shape of primary particles and their state of

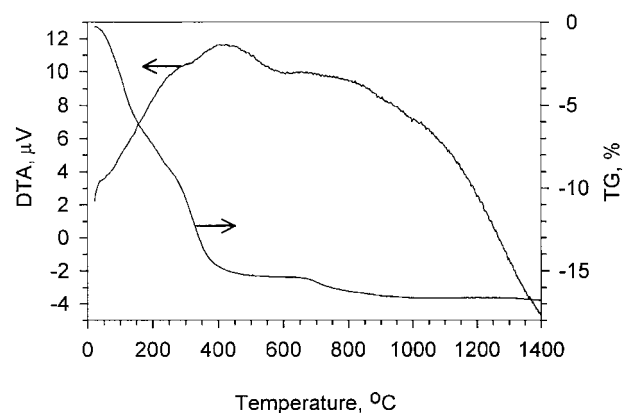


Fig. 2. DTA/TG analysis of powder precipitated with  $\text{H}_2\text{O}_2$ .

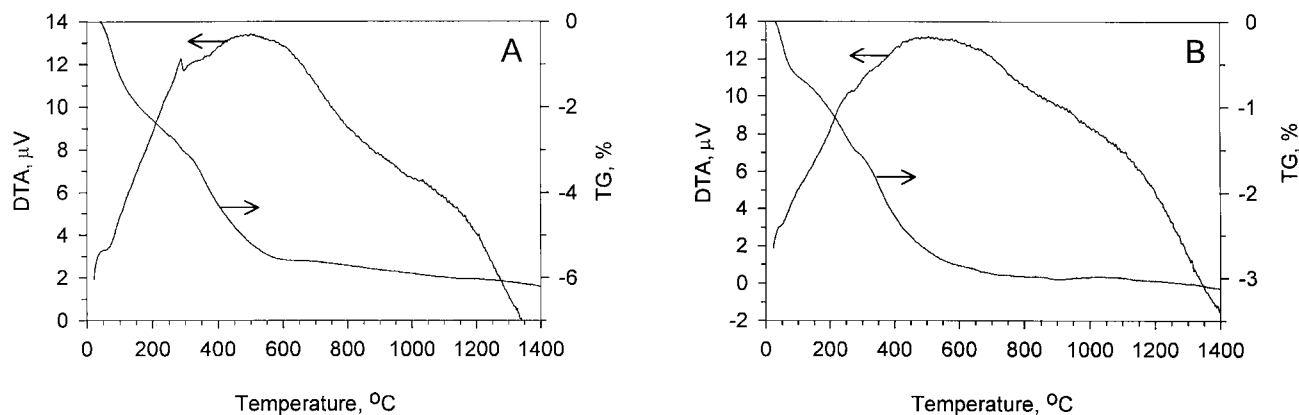


Fig. 1. DTA/TG analysis of powder precipitated with  $\text{NH}_4\text{OH}$ : (A) not autoclaved; (B) autoclaved at 180°C for 4 h.

agglomeration. The general morphology of the particles precipitated by ammonium hydroxide is shown in Fig. 4(A). The precipitate consisted of non-uniform agglomerates of equiaxed crystallites approximately 3–4 nm diameter. On calcination there was considerable grain coarsening and the agglomerates were hard and non-dispersible Fig. 4(B). Hydrothermal treatment of the hydroxide precipitate resulted in non-agglomerated uniform cubic crystallites 15–20 nm in diameter as shown in Fig. 4(C). The hydrothermally treated powder exhibited considerable coarsening of crystallite size after calcination for 1 h at 300°C [Fig. 4(D)].

Particles obtained by precipitation with hydrogen peroxide at room temperature consisted of dense agglomerate of crystallites 3–4 nm in diameter as shown in Fig. 5(A) and (B). Crystallisation of cerium oxide could be observed under the electron beam during TEM examination. Figure 5(C) and (D) shows particles produced by precipitation with hydrogen peroxide at 5°C. The crystallites were slightly smaller at 2–3 nm than in the sample precipitated at room temperature. Figure 5(E) and Fig. 5(F) show particles precipitated by hydrogen peroxide at 85°C. The densely-packed equiaxed agglomerates of 50–100 nm diameter that were

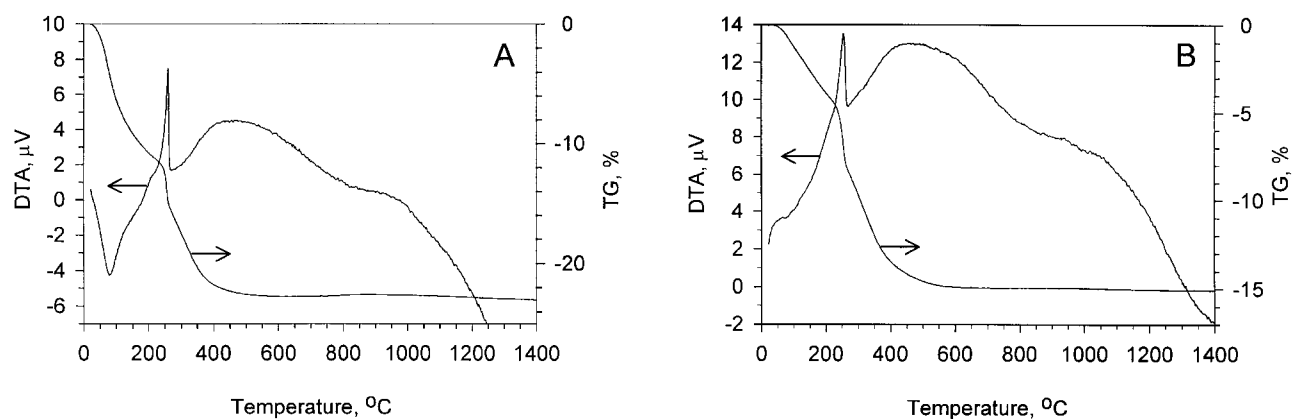


Fig. 3. DTA/TG analysis of powder precipitated with H<sub>2</sub>O, and NH<sub>4</sub>OH: (A) as prepared, (B) after 4 h at 100°C.

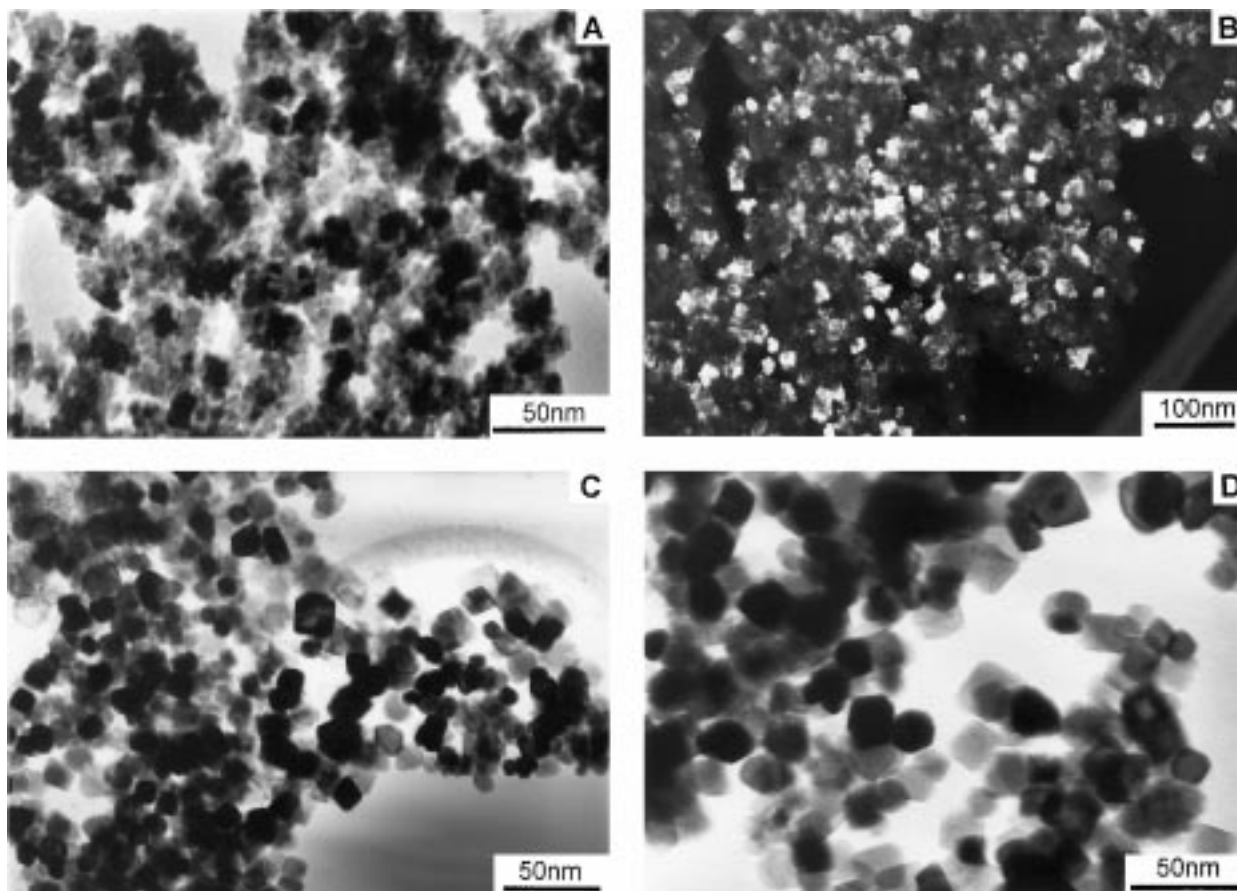
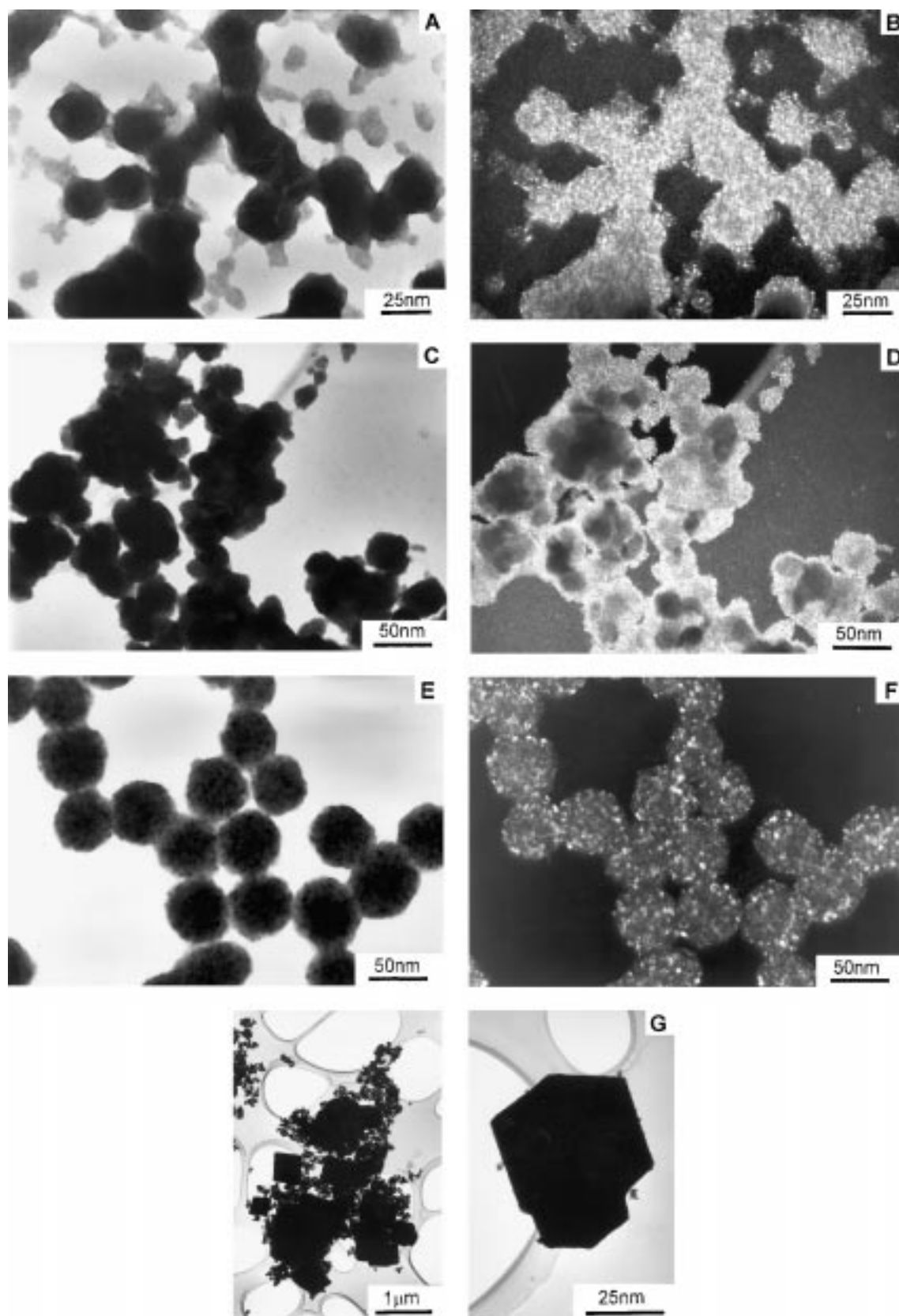


Fig. 4. TEM images of powders precipitated with NH<sub>4</sub>OH. Precipitate dried at 85°C; (A) precipitate calcined for 1 h at 500°C; (B) dark field. (C) Powder after hydrothermal treatment for 4 h at 180°C. (D) Hydrothermally treated powder after calcination for 1 h at 300°C.

obtained are typical of agglomerates formed during homogeneous precipitation and consisted of randomly oriented primary crystallites of 3–4 nm, i.e. similar in size to those precipitated at RT. Crystallite size coarsened considerable on calcination. Sharply-

faceted crystallites as large as the agglomerates were observed after 1 h at 300°C [Fig. 5(G)].

Particles from the two-stage precipitation at 5°C with hydrogen peroxide and ammonium hydroxide are shown in Fig. 6(A) and (B) for powder dried at

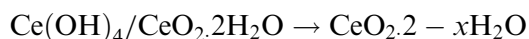


**Fig. 5.** TEM images of powders precipitated with  $\text{H}_2\text{O}_2$ . Precipitate formed at room temperature; (A) bright field, (B) dark field. Precipitate formed at 5°C: (C) bright field, (D) dark field. Precipitate formed at 85°C; (E) bright field, (F) dark field. (G) Precipitate calcined at for 1 h 300°C.

120°C for 2 h. The agglomerate structure was much less densely packed than in the samples precipitated with H<sub>2</sub>O<sub>2</sub> alone and consisted of randomly-oriented uniform crystallites 5–8 nm in diameter. The powder obtained from this sample after hydrothermal treatment is shown in Fig. 6(C) and Fig. 6(D). The crystallites were uniform and about 5 nm in diameter and appeared to be loosely agglomerated. After calcination for 1 h at 300°C there was very little change in crystallite size.

#### 4 Discussion

We investigated three methods of synthesis of CeO<sub>2</sub> powders and a variety of powder properties were obtained. The reference product in this work was powder produced by method A i.e. the precipitation of cerium hydroxide from Ce(III) nitrate by the addition of ammonium hydroxide. The XRD spectra of the precipitate dried at 80°C showed that the product consisted of well-crystallised CeO<sub>2</sub> and TG weight loss measurement indicated it to be slightly hydrated, so that a transformation must have occurred on drying the powder, e.g.:



This method yielded agglomerates with a wide size distribution and which were hard and non-dispersible after calcination and therefore not suitable for further processing. However, hydrothermal treatment of the wet precipitate yielded weakly-agglomerated cubic crystallites that were suitable for further processing. The crystallite size was 15–20 nm in size according to TEM images and about 27 nm according to XRD peak broadening. The hydrothermal treatment therefore solved the problem of hard agglomerates with this material, but at the expense of considerable crystal growth. In contrast, method C yielded a weakly-agglomerated powder which was not subject to crystal growth during hydrothermal treatment and which had a crystallite size of about 5 nm according to XRD measurement and which appeared somewhat smaller in TEM images, although the image magnification was too low for an accurate measurement.

A key feature of the method C was to mix together hydrogen peroxide and cerium(III) nitrate solution at a temperature low enough to prevent immediate reaction, e.g. about 5°C. Maintaining the solution at a constant low temperature ensured that subsequent precipitation occurred homogeneously and that a stable sol formed. The 0.1 M cerium(III) nitrate solution was acidic with a pH of about 4.3

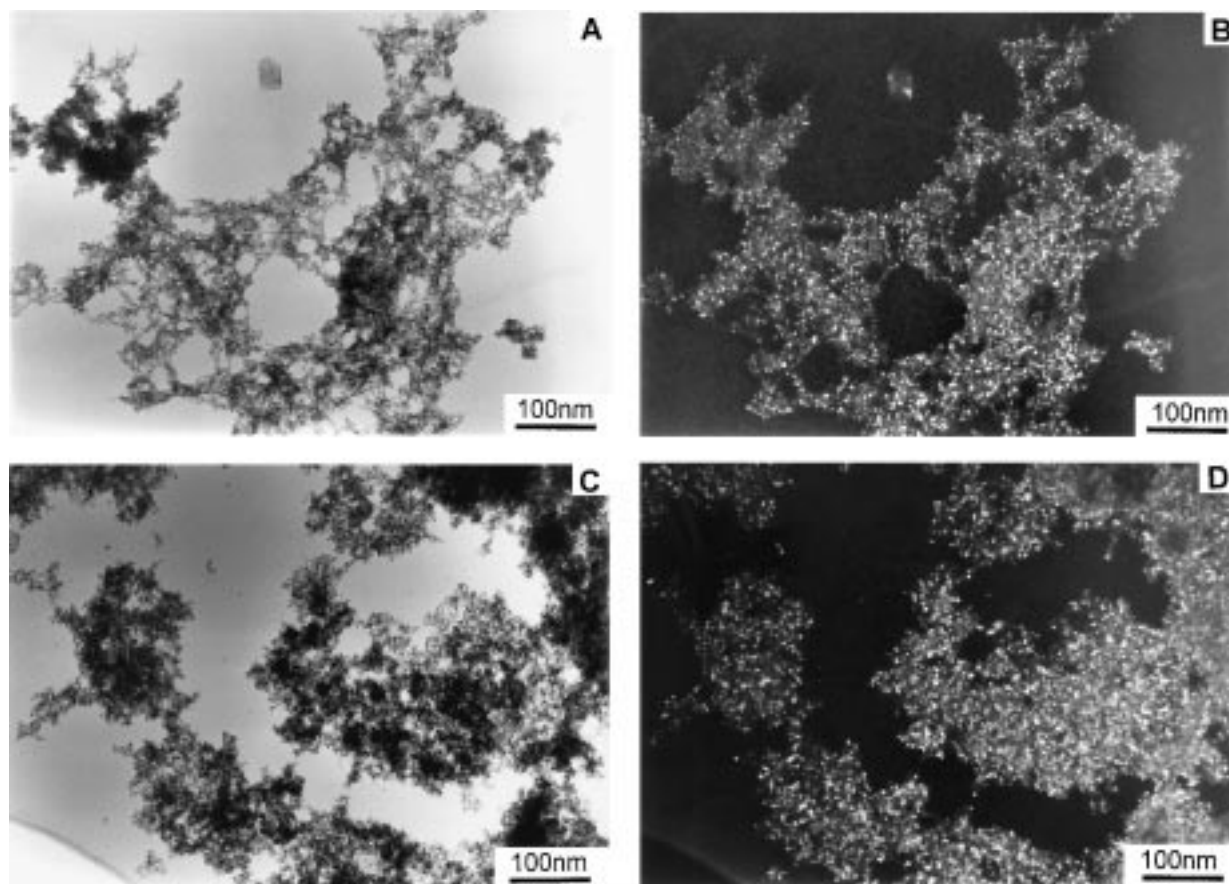
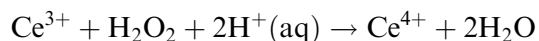


Fig. 6. TEM images of powders precipitated with H<sub>2</sub>O<sub>2</sub> and NH<sub>4</sub>OH. Precipitate dried at 85°C; (A) bright field, (B) dark field. Powder after hydrothermal treatment for 4 h at 180°C; (C), bright field (D), dark field.



and the oxidation of Ce(III) to Ce(IV) in solution is assumed to take place by:



with the formation of a sol of unknown composition. Weight loss measurements and a knowledge of the chemistry of cerium(IV) in solution allow us to suggest a possible composition. Ce(IV) in solution is a smaller ion with a higher charge than Ce(III) and so it is more easily hydrolysed and it readily forms many different complex ions. The formation of complex ions affects the  $E^0$  potential of the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  couple in acid solutions, varying, for example, from 1.44 V in 1 M  $\text{H}_2\text{SO}_4$  to 1.70 V in 1 M  $\text{HClO}_4$  because of the different anion species present. The strong tendency of Ce(IV) to form complex ions may have resulted in the formation of a complex between  $\text{Ce}^{4+}$  and  $\text{OOH}^-$  species resulting in partial precipitation. Lanthanide peroxides are known to exist, but they are not well-characterised because they are difficult to isolate in pure form. They appear to be intermediate in character between the strongly ionic alkali metal peroxides which form well-crystallised hydrates and the strongly covalent peroxides of Zn, Cd and Hg.

The composition of the dried sol particles precipitated with  $\text{H}_2\text{O}_2$  alone (method B) as deduced from TG was  $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  (measured weight loss = 16.8%, theoretical weight loss = 17.3%). Precipitation of a hydroxide in an acidic solution seems unlikely, but it could form during the drying procedure due to the limited stability of lanthanide peroxides. The crystallite size of about 3 nm is also an indication that the precipitation mechanism differed from that with ammonium hydroxide which yielded crystallites about 5 times larger. The role of the peroxy ligand during precipitation may have been to reduce the crystallite growth rate by changing the surface properties or morphology of the particles.

Addition of ammonium hydroxide to the sol (method C) resulted in further precipitation of cations from solution to yield an orange precipitate for which a composition of  $\text{Ce}(\text{OH})_3\text{OOH}$  was deduced from TG (measured weight loss = 23%, theoretical weight loss = 23.2%). This was the composition deduced for the dried product but, given the uncertainty about the stability of the lanthanide peroxides, it may be more appropriate to describe the precipitate that formed in solution by the general formula  $\text{Ce}(\text{OH})_{4-x}\text{OOH}_x$  with  $x = 1$  for the precipitate formed at 5°C. The  $x = 1$  composition appeared to be stable enough to withstand drying at 80°C but did not withstand 4 h at 100°C.

The use of ammonium hydroxide in the second stage of method C not only completed the precipitation process of method B but also disrupted the dense

agglomerates formed by  $\text{H}_2\text{O}_2$  precipitation as can be seen by comparing Fig. 5 and Fig. 6. Loosely-agglomerated powder should be less subject to crystallite growth on calcination in proportion to the reduced number of contact points between crystallites. Crystallite growth was insignificant during hydrothermal treatment of samples precipitated with hydrogen peroxide and ammonium peroxide, and the crystallite size remained under 5 nm. In samples precipitated with ammonium hydroxide alone, crystallite size almost doubled to over 25 nm under the same conditions. It is difficult to attribute the suppression of crystallite growth during hydrothermal treatment to the continued presence of the peroxy group, which is believed to be unstable at the temperatures used i.e. 180°C. The addition of ammonium hydroxide in method C therefore appears to be an important factor in the prevention of hard agglomerates which might otherwise transform to single crystals on heating as shown in Fig. 5(G). Crystallites smaller than 5 nm were reported previously only in the case of precipitation of  $\text{CeOSO}_4 \cdot \text{H}_2\text{O}$  from Ce(IV) sulphate solution.<sup>6</sup> In contrast to the nitrate group, the sulphate group is not easily decomposed on calcination, and sulphate is therefore generally not acceptable in a ceria precursor.

The method of inducing homogeneous precipitation by the oxidation of the cation to a higher valence state with an increased hydrolysability, in this case Ce(III)/Ce(IV), is also applicable to other materials, e.g. Fe(II)/Fe(III). An advantage of using of hydrogen peroxide as an oxidising, complexing and precipitating ligand is that it decomposes readily and therefore does not contaminate the end product with additional anion species.

## 5 Summary and Conclusions

The properties of cerium oxide are sensitively dependent on the method of preparation and the objective of this work was to obtain small crystallites without forming hard agglomerates. For this purpose neither ammonium hydroxide nor hydrogen peroxide alone was a suitable precipitating agent. We succeeded in preparing weakly-agglomerated ceria powders with a crystallite size of under 5 nm from Ce(III) nitrate solution by the addition of hydrogen peroxide at 5°C to slowly oxidise the cation to a higher valence state and thereby initiate homogeneous precipitation with the formation of dense spherical agglomerates. The precipitation process was then completed by the addition of ammonium hydroxide which also disrupted the spherical agglomerates leaving a weakly-agglomerated powder. The process was completed by hydrothermal

treatment at 180°C without increase in crystallite size. The weakly-agglomerated state of the ceria powder, the uniform crystallite size of under 5 nm, and the absence of deleterious anion impurities are characteristics which make the powder suitable for a variety of ceramic forming processes.

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