

Lattice Constant Dependence on Particle Size for Bulk and Doped Ceria prepared from a Citrate Sol-Gel

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ABSTRACT

High surface area ceria nanoparticles have been prepared using a citrate sol-gel precipitation method. Changes to the particle size have been made by doping ceria powders, and calcining at different temperatures. X-ray methods were used to determine their lattice parameters. The particle sizes have been assessed using transmission electron microscopy (TEM) and the lattice parameter found to fall with decreasing particle size. The results are discussed in the light of the role played by surface tension effects.

Keywords: ceria, precipitation, lattice strain, d-spacing, surface tension effects.

1 INTRODUCTION

Ceria (and doped ceria) has become one of the most important ceramic materials. It has a number of important and varied catalysis uses (most notably as an important component of the three way automotive catalyst) [1], as an ionic conductor [2], as a gas sensor [3], and as an electrolyte material of solid oxide fuel cells [4]. Ceria thin films have also found uses as high refractive index materials and insulating films on semiconductors. Nanoparticles, in general, show higher catalytic activity, better sinterability, for example, by comparison with coarse grained bulk materials [5].

The defect chemistry of ceria is relatively well established. It is generally thought that as a trivalent cation is added to the lattice, its charge is compensated by the presence of anion vacancies. Such vacancies are associated with the dopant cations and are randomly distributed on anion sites within the fluorite lattice. In particular, whilst this maybe thermodynamically, the most important defect mechanism, other defect systems are possible as minority species [6] and experimental evidence for interstitial oxygen defects has been found for nanoparticles of ceria [7]. The change in lattice constant of ionic crystallites with decreasing nanoparticle size is an important issue that is not fully understood [8]. Tsunekawa et al report lattice expansion with decreasing particle size for several

nanosized CeO₂ particle preparations [9]. The results were from conventional electron diffraction performed in a TEM. Usually TEM diffraction patterns cannot provide the accuracy required of lattice parameter measurements, which need to be better than 0.5%. More definitive measurements of this changing lattice constant are presented here using x-ray diffraction.

There are numerous chemical methods for the production of nano-dimensioned particles of ceria. These include precipitation, sol-gel techniques, micellar controlled (nanoreactors) and oxidation. Most syntheses of ceria nanoparticles aim to provide spherical particles of high surface area, which are either non-agglomerated or weakly agglomerated. However, each preparation method will produce materials with different defect densities and morphologies and it is difficult to relate any changes to variations in particle dimensions. For this investigation, the citrate sol-gel precipitation approach was employed, which yielded high surface area ceria nanoparticles.

2 SYNTHESIS TECHNIQUES

25ml of ammonium hydroxide is slowly added to 100ml 1 molar solution of Ce(NO₃)₃·6H₂O to precipitate out the CeO₂ under constant stirring. This results in a thick yellow/white emulsion, which is left to further stir for 30mins before being vacuum dried in a Buchner funnel. The brownish/ purple precipitate is dried at 60°C for 24 hours. A 10:1 molar ratio of lanthanum (La) to cerium is used for dopant inclusion purposes. The preparation of the acid-precipitated gel samples require 3g of the above un-doped or doped ceria powder to be weighed out into a sample vial. 3ml of 70% citric acid is then added to both ceria samples. This mixture is allowed stir for 12 hours. This is repeated for 3ml nitric acid and 3ml oxalic acid, using 3g of doped and un-doped ceria powder for each, for comparative purposes. After stirring, the acid peptised emulsions are dried at 80°C for 12 hours. The precipitation samples are calcined at different temperatures up to 1000°C with dwell times of 2.

Powder x-ray diffraction (PXRD) profiles were recorded on a Philips 3710 PWD diffractometer (θ - 2θ mode), equipped with a Cu K α radiation source and

standard scintillation detector. Particle sizes were determined from x-ray results using the Scherrer equation. Surface areas were measured using Nitrogen adsorption/desorption analysis on a Micrometrics Gemini 2375 instrument at 77K. Samples were degassed at 200°C for 24hrs using ultra high grade 5.0 nitrogen prior to each measurement. TEM was used for structural characterization. Each powder was dispersed onto holey carbon support grids and examined at 200kV in a JEOL 2000FX.

3 RESULTS

At high temperatures, ceria, of cubic fluorite structure, is susceptible to crystalline growth. Low temperature sintered ceria exhibits broad and low intensity PXRD peaks. From these PXRD patterns, lattice parameter and particle size approximations can be calculated. The lattice parameter for the ceria fluorite structure is 0.541nm. Low temperature ceria tends to exhibit higher lattice parameters due to the presence of defects and impurities. Such defects are introduced during sample preparation and vary according to method and reagents used. Figure 1 and 2 illustrates D-spacing as a function of sintering temperature, for both the un-doped and doped ceria.

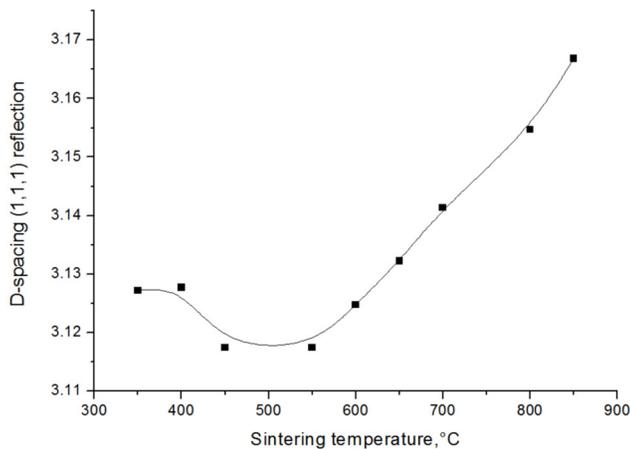


Figure 1: D-Spacing (Å) as a function of Sintering Temperature for un-doped ceria.

The percentage increase in d-spacing for un-doped ceria is approximately 3%, whereas for the La doped ceria this increase is only approximately ½%. Literature suggests that lattice parameter and particle size are directly related, stating that, as particle size increases this causes a corresponding decrease in lattice parameter. However, from the experimental technique employed here, particle size increases as temperature increases, though lattice parameter continues to increase steadily.

As measured with TEM, the particle or grain size of the oxide can be seen for both un-doped and doped ceria samples, and an average value was obtained from the measurement of 100 grains in each powder. For un-doped

ceria, at 350°C, the average particle size is 29.8nm which increases to 54.9nm when calcined to 950°C. At 650°C, an average particle size of 25.7nm is measured, which is not too dissimilar from the 350°C sample. In direct comparison to this, for La doped ceria, at 350°C, the average particle size is only 10.0nm, which undergoes only a marginal increase when calcined to 950°C, where the average grain size only goes up to 28.3nm.

Figure 3 and 4 shows TEM dark field micrographs of un-doped and doped ceria nanoparticles at A)350°C, B)650°C and C)950°C respectively. The Scherrer equation calculations are broadly in line with this TEM analysis.

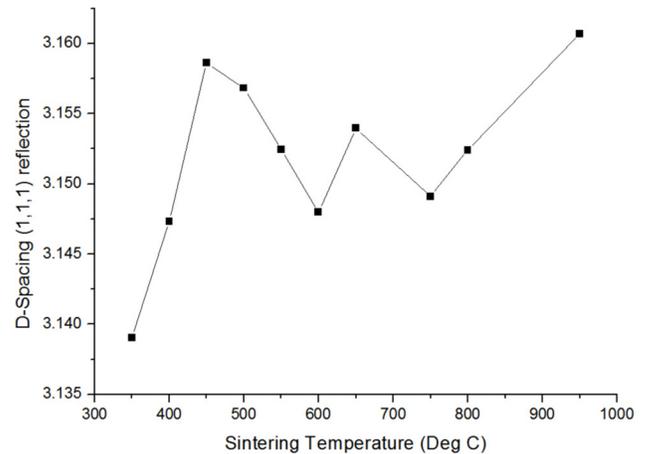


Figure 1: D-Spacing (Å) as a function of Sintering Temperature for doped ceria.

4 DISCUSSION AND CONCLUSIONS

The reason for lattice contraction at small particle sizes is considered. One might imagine that at small particle sizes where poor structural order and high defect concentrations are possible that expansion of the lattice might be observed through the presence of large Ce^{3+} ions within the lattice. However, as observed by PXRD/TEM, strong lattice **contractions** (not expansions) were measured with decreasing particle size. These observations strongly indicate surface tension plays a major role in determining the lattice parameter. The effect of dopant 3+ ion inclusion should also be considered.

It should be noticed that there is no significant increase in the lattice parameter as a function of dopant inclusion. However, in view of the relatively low loadings and the variation of size with temperature this is not too surprising. More unexpected is the lower dependence of the lattice structure and size with calcination temperature (i.e. particle size). As stated previously, the percentage increase in d-spacing for un-doped ceria is approximately 3%, whereas for the La doped ceria this increase is only approximately ½%. It should firstly be noted that, as measured with TEM and XRD, the particle size of La doped ceria does not

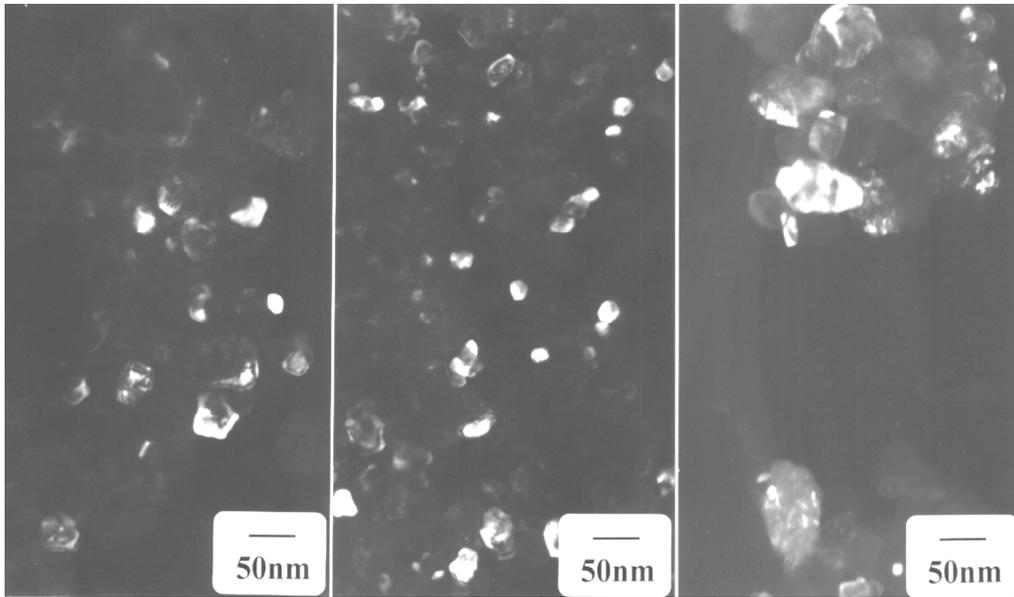


Figure3: Dark field TEM micrograph of un-doped ceria nanoparticles at 350°C, 650°C and 950°C.

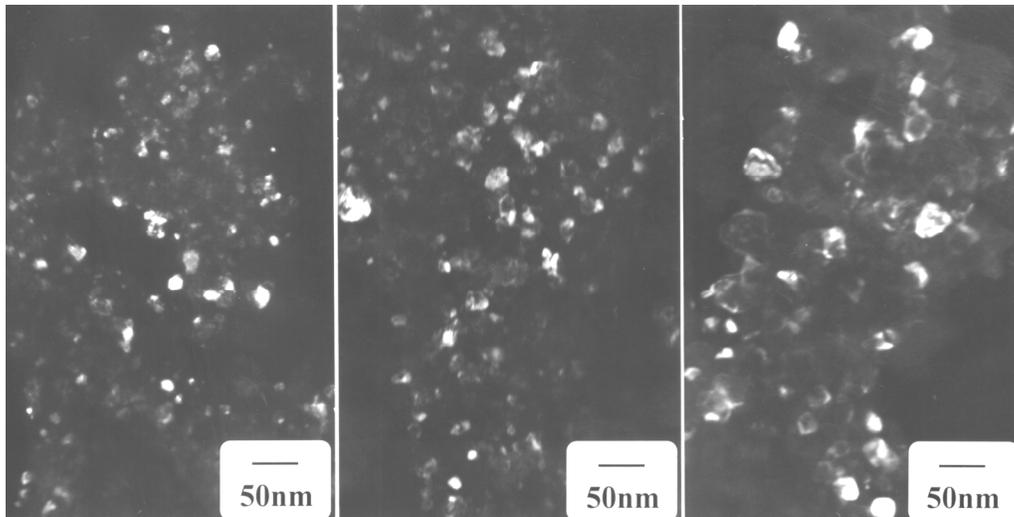


Figure3: Dark field TEM micrograph of doped ceria nanoparticles at 350°C, 650°C and 950°C.

increase as significantly as the un-doped samples as the temperature is raised. This observation, and the smaller dependence of lattice parameter with size, can be explained by increased rigidity of the lattice resisting external surface tension effects and thermally induced sintering. This increased rigidity may be attributed to the following: increasing lattice strain results from the fact that La³⁺ ions, which substitute for Ce⁴⁺ ions, are considerably larger in size. The presence of these substitutionally derived lattice strain effects is the direct cause of the rigidity.

The data presented here further suggests, that anion vacancy defects are not created to any major extent in un-doped ceria in this temperature and size range, since if this was the case, we would expect the doped and un-doped systems to be similar and also lattice expansion to be dominant (at small particle sizes). It is clear that the careful investigation of lattice parameter changes versus particle size, coupled to very careful synthesis methods, can provide a deeper understanding of oxide particle nanoscience.

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