Lattice Constant Dependence on Particle Size for 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 calcining the ceria powders at different temperatures, and X-ray methods 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.

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) \cite{1}, as an ionic conductor \cite{2}, as a gas sensor \cite{3}, and as an electrolyte material of solid oxide fuel cells \cite{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 \cite{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 the thermodynamically the most important defect mechanism, other defect systems are possible as minority species \cite{6} and experimental evidence for interstitial oxygen defects has been found for nanoparticles of ceria \cite{7}.

The change in lattice constant of ionic crystallites with decreasing nanoparticle size is an important issue that is not fully understood \cite{8}. Tsunekawa et al report lattice expansion with decreasing particle size for several nanosized CeO\textsubscript{2} particle preparations \cite{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. Experimental Details.
25ml of ammonium hydroxide is slowly added to a 1 molar solution of Ce(NO$_3$)$_3$·6H$_2$O to precipitate out the CeO$_2$ 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. The preparation of the acid-precipitated gel samples require 3g of the above bulk ceria powder to be weighed out into a sample vial. 3ml of 70% citric acid is then added to the bulk ceria. This mixture is allowed stir for 12 hours. This is repeated for 3ml nitric acid and 3ml oxalic acid, using 3g of bulk 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 hours.

Powder x-ray diffraction (PXRD) profiles were recorded on a Philips 3710 PWD diffractometer ($\theta$–2$\theta$ mode), equipped with a Cu K$\alpha$ 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. Figure 1 is a PXRD 2D comparison plot of various temperatures (350°C to 1000°C) for the citrate technique outlined above.

![Figure 1: 2D PXRD comparison plot for the citric acid method.](image-url)
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 2 illustrates d-spacing as a function of sintering temperature. 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 each sample and an average value was obtained from the measurement of 100 grains in each powder. At 350°C, the average particle size is 29.8nm by comparison with 950°C where the average grain size goes up to 54.9nm. At 650°C, an average particle size of 25.7nm is measured, which is not too dissimilar from the 350°C sample. Figure 3 shows TEM dark field micrographs of ceria nanoparticles at A)350°C, B)650°C and C)900°C respectively. The Scherrer equation calculations are broadly in line with this TEM analysis.

![Figure 2: Surface area as a function of sintering temperature. Lattice constant as a function of sintering temperature.](image)

![Figure 3: Dark Field TEM micrographs of ceria nanoparticles at 350°C, 650°C and 900°C.](image)
4. Discussion and Conclusions
The reason for lattice contraction is considered. Results obtained from PXRD analysis illustrate that since the lattice parameter and temperature range are equivalent, as the lattice parameter increases as a function of the annealing temperature, defects such as anion vacancies decrease.

As observed by PXRD, strong lattice *contractions* (not expansions) were measured with decreasing particle size, strongly indicating surface tension plays a major role in determining the lattice parameter. The data suggests that anion vacancy defects are not created to any major extent in this work. This investigation of lattice parameter changes versus particle size, coupled to very careful synthesis methods, provides a deeper understanding of oxide particle nanoscience.

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