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# The effect of the calcination process on the crystallite shape of sol–gel cerium oxide used for glass polishing

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Pure cerium oxide was produced via the sol–gel process, which allowed an investigation into the effect of thermal heat treatment on its crystallite shape and size. Transmission electron microscopy (TEM) and X-ray diffraction studies demonstrated that the actual crystallite shape changed with increasing calcination temperature. At a temperature of 850 °C, truncated octahedral crystallites were produced which display a greater area of close packed planes of cerium atoms on the surface, compared to those calcined at lower temperatures. Cerium oxide that had undergone calcination at 850 °C is also very effective as a glass-polishing medium. Because the calcination process effects both the shape of the crystal and its size at this temperature, it is proposed that polishing efficiency is predominantly determined by the higher incidence of cerium atoms that can be presented to the glass surface.

## 1. Introduction

It has long been known and believed that the crystallite size of cerium oxide glass-polishing compounds is critical with regards to the ability of such compounds to polish glass. It has been observed that the crystallite size, as measured by X-ray diffraction, increases with calcination temperature [1]. However, recent research into glass-polishing mechanisms has revealed that, in addition to size, the shape of the individual crystallites may be the controlling factor [2]. The mechanism of glass removal from the bulk is a mechano-chemical process, involving chemical reactions such as complex Ce–$SiO_2$ bonding, and mechanical effects such as abrasion and plastic flow of the glass surface during polishing. The proposed mechanisms have been reviewed elsewhere [3]. In this paper we present results of the effect of calcination conditions on cerium oxide crystallites. In order to measure accurately the crystallite size, the cerium oxide powders were produced by the sol–gel process, enabling high-purity polishing powders, free from other rare-earth elements, to be employed.

## 2. Experimental procedure

Cerium oxide was obtained in the form of dry gel powder made under precipitation conditions. This was manufactured from a cerium oxide sol (colloid suspension of cerium oxide primary particles) which had been passed into a drying chamber of a spray drier. In the absence of gravity and other external stress fields, surface tension causes the droplets of any liquid to assume a spherical shape. However, as a droplet is atomized in the spray drier, there are also dynamic external stresses applied to the droplet that can overcome the surface tension effects and deform the droplet shape. In the present case, gel particles became "doughnut" shaped. This results from the addition of nitric acid to the sol prior to spray drying, thus lowering the surface tension which can then be outbalanced during the drying process. Fig. 1 illustrates the formation mechanism of these "doughnut" shapes, with the up-flow of hot air and downward force as a result of gravity causing the shape of the droplet to oscillate until it collapses. The underside of the droplet is subject to a hotter air temperature, causing faster evaporation through this surface. This eventually leads to a layer with a higher viscosity pulling the trailing surface inwards to assist in the collapse of the droplet. As the droplet travels down the spray drier, water will evaporate to form a dry free-flowing gel particle [4]. This approach enabled particles of a controlled morphology and size to be obtained with excellent repeatability (Fig. 2).

The cerium oxide powders were subsequently calcined in air on a silica tray at various temperatures for 1800 s. The powder size and morphology were observed by the use of scanning and transmission electron microscopy. The powders were mounted on aluminium stubs, in the case of scanning electron

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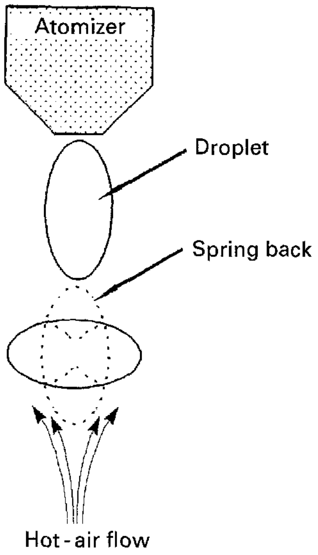

*Figure 1* Schematic diagram showing spring-back of sol droplet due to surface tension and the up-flow of hot air [4].

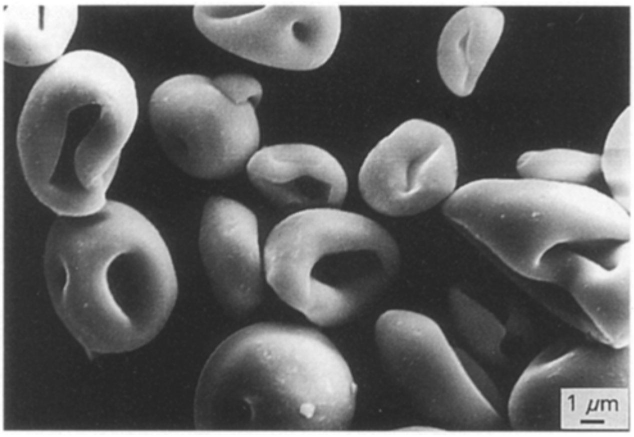

*Figure 2* Scanning electron micrograph of calcined cerium oxide gel produced via the sol–gel process. The sol was spray dried, which controlled the particle size and morphology.

microscopy, and on copper grids with an amorphous carbon film for transmission electron microscopy. The crystallite size of the powders was measured by X-ray diffraction line broadening. Using a computer data acquisition program, it was possible to obtain an accurate measurement of the individual peak width and 2θ. This was computed using the Scherrer equation [5]

$$t = \frac{K\lambda}{B\cos\theta_B} \qquad (1)$$

where $t$ is the average crystallite dimension, $K$ is the shape constant (for cubic structures, a value of 0.9 was used), $\lambda$ is the wavelength of the X-ray, $B$ is the breadth of the peak, and $\theta_B$ is the angle of the peak centre.

## 3. Results

X-ray diffraction plots of cerium oxide gel before calcination (Fig. 3) and after 1800 s at 850 °C (Fig. 4) illustrate the effect of temperature on the half-height line broadening. The use of transmission electron microscopy visually proved that there was a change in crystallite shape and size. Fig. 5 shows 5 nm diameter loosely bonded crystallites of a very narrow size distribution, and Fig. 6 that of larger 80 nm crystallites that are strongly bonded together, which had been produced at two different temperatures. The {2 0 0} and {1 1 1} atomic planes are the most prominent. Using the relative intensity of the X-ray lines of these planes, a simple ratio can be calculated (Table I). With increasing calcination temperature the individual gel particles densify along with an increase in crystallite size (Fig. 7).

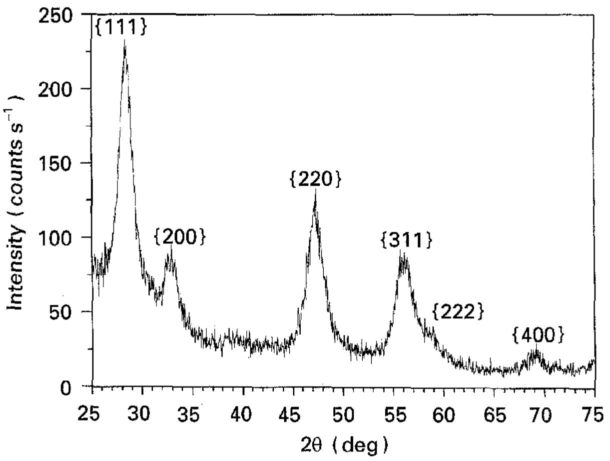

*Figure 3* X-ray diffraction plot of cerium oxide gel, before calcination.

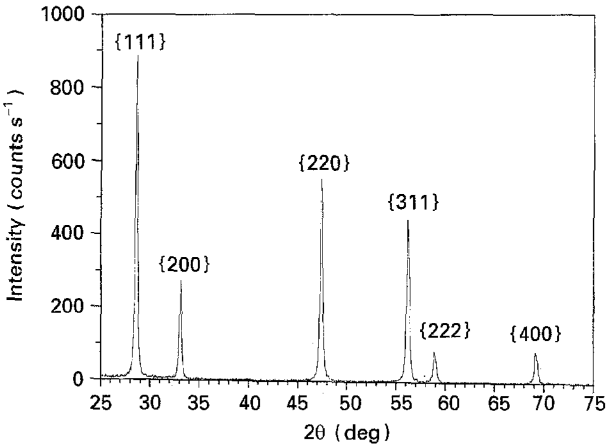

*Figure 4* X-ray diffraction plot of cerium oxide gel calcined at 850 °C for 1800 s.

## 4. Discussion

The initial dried gel particles consist of crystallites with an approximate size of 5 nm (Fig. 8). The random arrangement of these crystallites gives rise to a porous gel with a high percentage of structural water entrapped in the pores. During the early stages of calcination up to 500 °C there is very little change in crystallite size. However, there is a steady increase in density as water evaporates (Fig. 7) and an increase in the number of cross-links between crystallites. The calcination process also burns out stabilizers used in sol

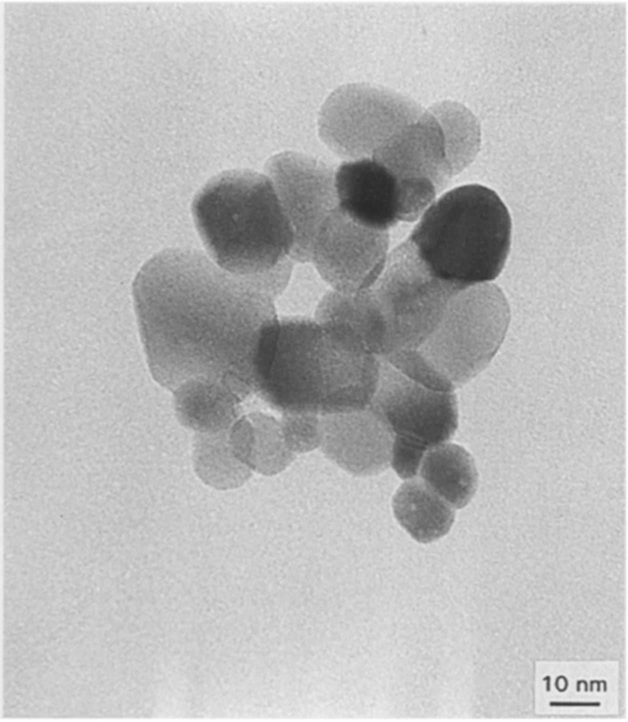

*Figure 5* Transmission electron micrograph of cerium oxide gel before calcination; approximate crystallite size of 5 nm.

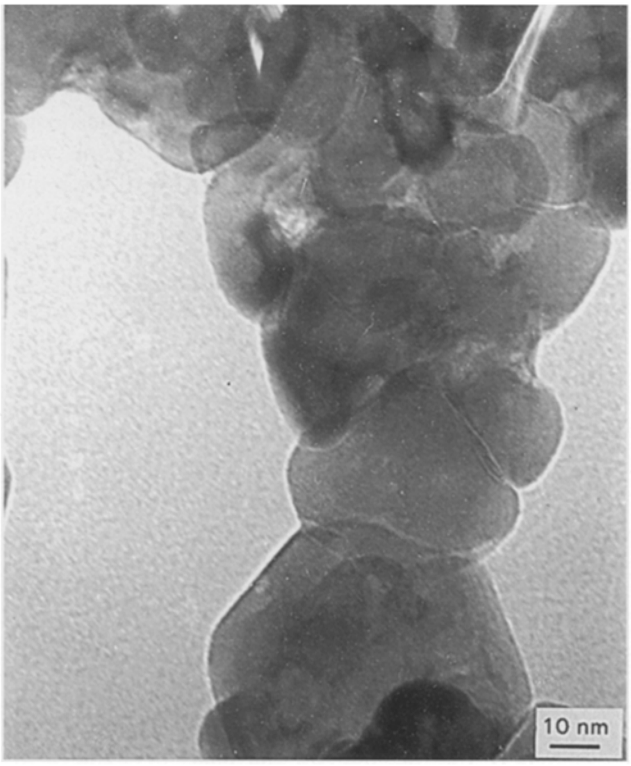

*Figure 6* Transmission electron micrograph of cerium oxide gel calcined at 850 °C for 1800 s, approximate crystallite size of 60 nm.

production, especially surface nitrates. The large surface area to volume ratio of the crystallites before calcination supplies a driving force for surface diffusion. As the sintering temperature is neared ( > 1200 °C), bulk diffusion occurs. There is no additional driving force for surface diffusion as the individual crystallites can be considered to be strain free.

TABLE I Comparison of the intensity ratio of the two most prominent planes of a cerium oxide crystallite, with increasing calcination temperature

| Calcination temperature (°C) | {2 0 0}/{1 1 1} intensity ratio |
|---|---|
| Gel (not calcined) | 0.41 |
| 500 | 0.37 |
| 800 | 0.33 |
| 1150 | 0.29 |

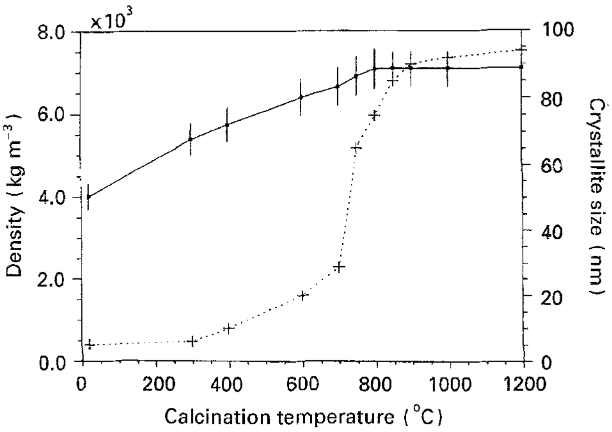

*Figure 7* (■) Density and ( + ) crystallite size of cerium oxide gel, calcined at various temperatures for 1800 s.

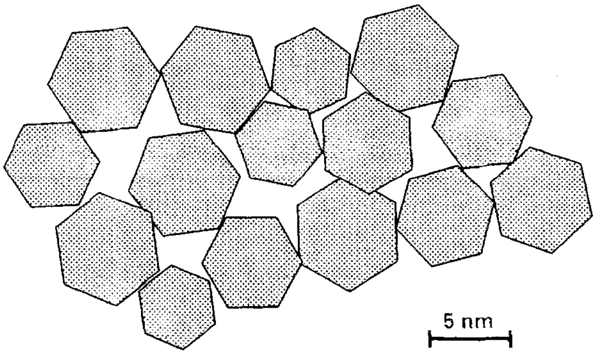

*Figure 8* Primary crystallites of approximately 5 nm diameter that make up the gel particle, before calcination.

Above 500 °C, the crystallite size starts to increase (Fig. 7) reaching a maximum at 900 °C. There is a 19% volume shrinkage during calcination of the gel particles due to the reorganization of the crystallites resulting in a higher stacking density (Fig. 6) after calcination. XRD results of the half-height width of the peaks shows an increase in crystallite size (Figs 3 and 4), and the crystal structure becomes more uniform. A simple relationship can be derived from these data relating the rate of growth of the crystallites, $\Delta C_r$, to the mean crystallite size, $C_s$, at a given temperature

$$\Delta C_r \propto \frac{1}{C_s} \qquad (2)$$

The growth of crystallites is not symmetrical, because the growth rate of the two prominent planes, {2 0 0} and {1 1 1} are not equal. XRD half-height peak

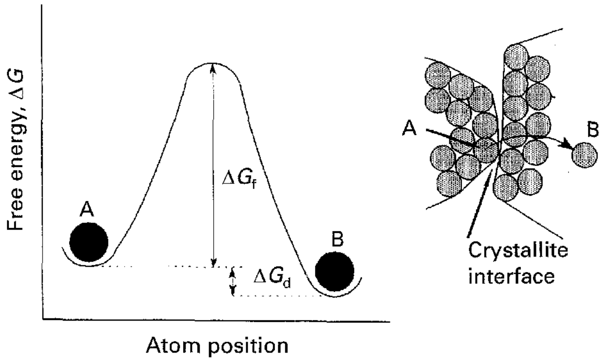

*Figure 9* Free energy of the diffusion of an atom (A) to a new site (B); $\Delta G_f$ is the free energy required to move the atom, $\Delta G_d$ the decrease in free energy after the atom has moved.

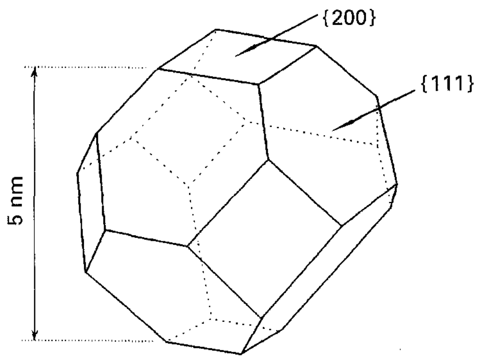

*Figure 10* Crystallite of gel calcined at 325 °C (not to scale with Fig. 11).

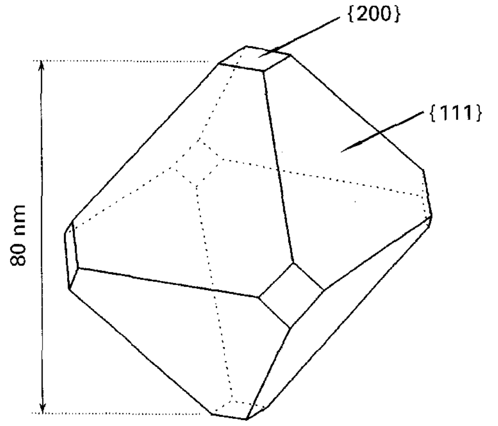

*Figure 11* Crystallite of gel calcined at 850 °C; the {1 1 1} planes have grown to a greater extent than {2 0 0} planes (not to scale with Fig. 10).

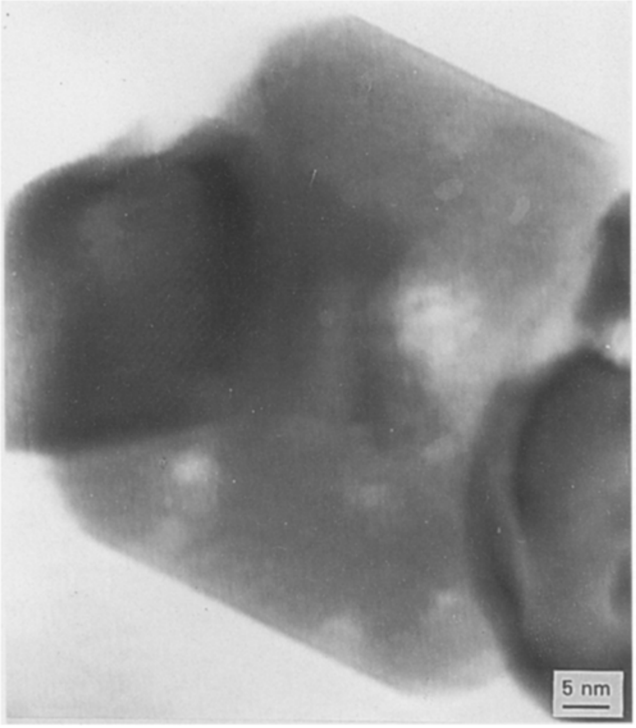

*Figure 12* Transmission electron micrograph of cerium oxide gel calcined at 850 °C for 1800 s, showing the shape of a single crystallite, 63 nm between {2 0 0} planes.

broadening allows calculation of the separation between crystallite faces, resulting in the establishment of a model of the actual shape of the crystallite. Table I shows the ratio of the intensity of {2 0 0} to {1 1 1} with calcination temperature, indicating the greater growth of the {1 1 1} planes. The accelerated growth of the {1 1 1} plane occurs because its free energy, $\Delta G_f$, is lower than that of the {2 0 0} planes as atoms migrate to the close packed {1 1 1} planes (Fig. 9). Duncan [6, 7] observed this phenomenon of accelerated plane growth in cerium oxide, but he did not pursue its relevance to glass polishing to any extent. Fig. 10 shows the predicted shape of a crystallite of the gel calcined at 325 °C, and Fig. 11 that of a crystallite of the gel calcined at 850 °C, where the {1 1 1} planes have grown at a faster rate than the faces of the {2 0 0} planes. This change in shape is confirmed by TEM studies (Fig. 12). Sufficient sampling was undertaken to certify that this change in crystallite shape was significant. All the crystallites do not grow to the same size because the internal crystallites are restricted by the presence of neighbouring crystallites. The internal crystallites grow to fill all vacant voids, resulting in a dense gel particle free from porosity. Surface crystallites have less restraint thus leaving them free to grow away from the bulk of the gel particle and reach the maximum size achievable under the calcination conditions. All crystallites observed were on the surface of the gel particles due to the difficulty of sectioning a 5 μm diameter gel particle. However, because surface crystallites are likely to be the only ones exposed to the glass surface during polishing these observations are significant.

At 1150 °C, {1 1 1} plane growth dominates (Table I). However, at this temperature the physical properties of the powder are unsuitable for a glass-polishing powder as the individual particles started to sinter together. It was decided on the basis of Table I to calcine at 850 °C, as this gave an effective glass-polishing powder and there was little to gain with a higher calcination temperature. The unit cell of cerium oxide is known to be face centred cubic (fcc), with an atomic arrangement of the *Fm*3*m* symmetry group [8]. Fig. 13 shows the configuration of the atom positions and in the present case the actual lattice parameter was measured from diffraction rings on the TEM to give $a = 0.53$ nm. Cerium atoms are located at the corners and faces of the unit cell with oxygen atoms in interstitial sites. The {1 1 1} planes are known to be

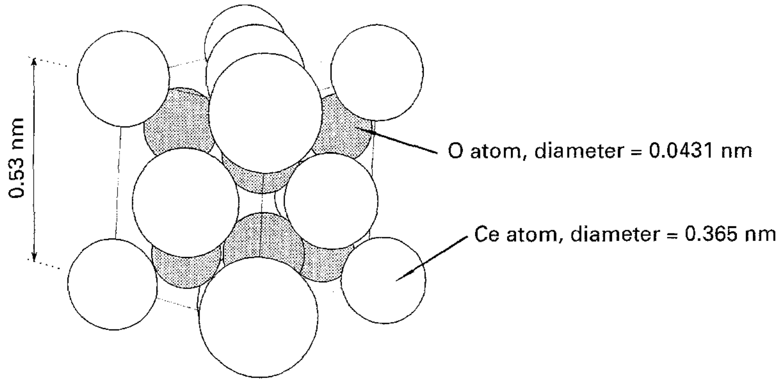

*Figure 13* Unit cell of cerium oxide, *Fm3m* symmetry group.

close packed, with 0.0082 atoms $nm^{-2}$, while $\{2\,0\,0\}$ planes have 0.0070 atoms $nm^{-2}$. Therefore, the calcination process which allows faster growth of $\{1\,1\,1\}$ planes exposes more cerium atoms on the surface of the crystallites.

## 5. Conclusion

Commercial glass-polishing powders are very irregular in size, morphology and composition. The sol–gel cerium oxide powder used in the present study was approximately 99.5 wt % pure with a regular particle size and morphology. This allowed controlled studies of its performance as a polishing compound. This consistency in composition ensured that the crystallite size and shape was repeatable under the same calcination conditions.

The calcination process modifies the shape of the crystallites by the faster growth of the close packed $\{1\,1\,1\}$ cerium-rich planes. It is believed that calcination of cerium oxide polishing compounds is necessary to achieve the desired crystallite shape, as distinct from merely increasing the crystallite size. With more cerium atoms exposed to the glass surface there are more reaction sites available during the polishing of glass and hence a faster rate of material removal occurs. It was found in glass-polishing experiments that cerium oxide calcined at 850 °C gave a very acceptable polishing compound that removed glass from the bulk with a high quality of surface finish ($R_a = 1.5$ nm).

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