Observation of a high pressure polymorph of titania by vibrational ball milling

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The observation of a high pressure polymorph of titania, originating from an anatase phase, using high energy impact vibrational ball milling (HEIVBM) is reported here for the first time. The observed polymorph conforms to the reported high pressure modified phase of titania [orthorhombic, $\alpha$-PbO$_2$ (Pbcn) structure] developed by static high pressure and shock wave techniques. X-ray diffraction (XRD) and electron spin resonance (ESR) techniques are used to characterize the polymorph.

1. Introduction
Titanium dioxide occurs in nature in three crystalline forms, namely, rutile (tetragonal prisms), more rarely as anatase (tetragonal pyramids) and brookite (flat rhombic prisms). A fourth polymorph, having an $\alpha$-PbO$_2$ structure (orthorhombic), has been developed from the anatase [1-3], brookite [2, 3] and rutile [2-7] phases of titania by static high pressure and shock wave techniques. These four structures are characterized by 6:3 oxygen–titanium co-ordination in which Ti-O bonds are not of equal length. In each case, the basic structural element is a distorted TiO$_6$ octahedron, that shares edges with similar octahedra in the structure. The four structures differ in the degree of distortion of the basic octahedral and in the packing of the octahedra.

It has been shown recently that ball milling, apart from particle fracture, may induce lattice strain in hard metal carbides and ceramic oxides [8-11]. The effect was studied by X-ray line broadening techniques, where the broadening of the line profile obtained by milling was interpreted in terms of crystal size, strain and stacking faults. Since ceramics are known to be brittle, serious doubts have been raised regarding the interpretation of the results, and the broadening of the line profiles has often been attributed to particle size reduction alone. Sarkar and Towner [12] have shown, by both X-ray line broadening and electron microscopy studies, that ball milling introduces strain in alumina powders in the form of dislocations. However, formation of a high pressure phase by HEIVBM has not previously been reported.

Jameson and Olinger [5] observed, by X-ray diffraction studies, the direct transition of rutile to the $\alpha$-PbO$_2$ form by in situ static high pressure, high temperature. The dynamic phase transition noted by McQueen et al. [6] at substantially higher pressure was also of a form that was considerably denser than the reported orthorhombic phase. Simons and Dachille [2, 3] and Bendelany et al. [4] independently reported synthesis of "$\alpha$-TiO$_2$" by static pressing and heating of other titanium dioxide polymorphs for long periods of time. Linde and DeCarli [7] also reported a high pressure polymorph of titania [orthorhombic, $\alpha$-PbO$_2$ (Pbcn) structure] under shock wave pressures. These investigators have all reported somewhat different lattice parameters for the orthorhombic phase, the ranges are as follows: $a = 0.4515 - 0.4563$ nm, $b = 0.5464 - 0.5498$ nm and $c = 0.3900 - 0.4939$ nm; corresponding crystal densities vary from $4.33 \times 10^3$ to $4.37 \times 10^3$ kg m$^{-3}$.

A high pressure phase of TiO$_2$ was first prepared by Dachille and Roy [1] from an anatase phase at pressures ranging from 1.5 to 10 GPa and temperatures ranging from 25 to 500 °C, but the powder pattern was not indexed owing to the small number and poor quality of the diffraction lines; consequently, the structure type was not determined. They could not identify the other lines because the high pressure phase prepared from anatase was always intergrown with a short-range ordered phase which produced broad diffraction peaks. Linde and DeCarli [7] observed the polymorphic behaviour of titania under dynamic loading conditions. Single crystal and polycrystalline specimens (including powder compacts of various densities) of titanium dioxide have been subjected to shock wave pressures in the 15–100 GPa range. X-ray diffraction studies of specimens recovered after shocking at various pressures above 15 GPa have shown the presence of an orthorhombic phase in the $\alpha$-PbO$_2$ (Pbcn) structure. Yields of the new phase were at the order of 10–30% for all 98% dense rutile powder compacts shocked at pressures in the range 15–100 GPa. Whereas, single crystal rutile specimens shocked at pressures in the same range showed marked variability in the yield of the new phase; the yields appeared to roughly correlate with the orientation of the crystal with respect to the direction of shock propagation. Yields of the $\alpha$-PbO$_2$ phase as high as about 90% were obtained from [001]- and [1 1 1]-oriented rutile crystals shocked at 45 GPa.

Linde and DeCarli [7] also used ESR techniques to identify the developed orthorhombic phase. Their work on rutile titania under dynamic loading showed...
ESR spectra that fell into three general classes: class 1, for high density powder compacts shocked to 45 GPa, having a line at $g = 2.008$; class 2, for initially single crystals (both undoped and doped with 0.015 wt % $\text{Al}_2\text{O}_3$) shocked to 20 or 45 GPa, having lines at $g = 2.008$ and $g = 1.987$; class 3, for undoped initially single crystals shocked at 20 or 45 GPa, having a line at $g = 1.994$ located on a broad peak. They explained their results in terms of the surface-sensitive behaviour of single crystal and polycrystalline specimens (including powder compacts of various densities) of titanium dioxide subjected to shock wave pressure.

Observation of a high pressure titania polymorph, derived from an anatase phase, attained by HEIVBM is reported in this paper. The results are interpreted in the light of XRD and ESR studies.

2. Experimental procedure

A 10 g charge of anatase phase titania powder (British Drug House) of high purity (99%), with an average particle size of 270 nm, was dry ball milled for various time periods up to 100 h in a pure alumina cylinder, with an alumina cretid in a Glen Creston M280 vibratory mill. The ball was vibrated within the cylinder at an amplitude of 50 mm and a frequency of 20 Hz. The impact energy of the ball was calculated to be of the order of 0.02 J. It was noticed during ball milling that, with increasing milling time, the strained material tended to cake together to form a solid aggregate due to strong agglomeration of the titania particles. As a result, it was very difficult to accurately measure particle size with the particle size analyser, even after ultrasonication (frequency, 20 kHz) for 30 min. However, the particle size of different milled powders was calculated from surface area measurements using a Carlo Erba Instrument (Model-1750 Sorpty) using the single point method. Adsorption isotherms of the powders were obtained with nitrogen. The surface area of the titania powders at different milling times was measured at $5.7 \times 10^3$, $8.1 \times 10^3$, $14.2 \times 10^3$, and $13.3 \times 10^3$ m$^2$ kg$^{-1}$ for the 0, 32, 64, and 100 h samples, respectively, as shown in Fig. 1. From the figure it was found that surface area increases with increasing milling time, in agreement with results for $\text{Al}_2\text{O}_3$ shown by Sarkar and Towner [12]. The particle size, $d$, of the different milled powders mentioned above was calculated directly from the measured surface area, assuming that the particles were spherical

$$d = \frac{6}{\rho S}$$

where $d$ is the particle size, $\rho$ is the density of the titania powder (3.893 x 10$^3$ kg m$^{-3}$) and $S$ is the surface area per gram of material. The calculated particle sizes were 270, 190.3, 151.1 and 115.8 nm for the 0, 32, 64 and 100 h milled titania powders respectively, shown in Fig. 1. It was apparent that the initial drop in particle size due to fracture was rapid, slowing down eventually.

The following techniques were used to characterize the milled powders.

2.1. X-ray diffraction

The unmilled and milled (for various times) anatase titania powders were examined by X-ray diffraction. XRD spectra of the powders were recorded in a Philips X-ray diffractometer (Model PW-1730) fitted with a goniometer and provided with a nickel-filtered CuK$_\alpha$ line (0.154 178 nm) X-ray source. Slow scan (1/4\(^4\) min$^{-1}$) XRD spectrum was recorded in a Philips X-ray diffractometer (Model PW-1010), fitted as above, for detailed analysis of the broad band. Fig. 2 shows the various XRD spectra of titania powder after different milling times, while Fig. 3 shows the slow scan XRD spectrum for the sample milled for 64 h.

2.2. Electron spin resonance

The room temperature electron spin resonance (ESR) spectra of the unmilled and milled powders of titania were recorded in a Varian (Model E-line Century Series) X-band ESR spectrometer. The spectra were recorded using the following settings: central field set = 340 mT, microwave power = 5 mW, microwave frequency = 9.45 GHz. Fig. 4 shows the different ESR spectra of the sample.

3. Results

3.1. X-ray diffraction

The X-ray diffraction spectrum (Fig. 2a) of the unmilled titania powder showed prominent peaks at $d = 0.352, 0.243, 0.237, 0.233, 0.189, 0.169$ and 0.166 nm, which were characteristic of the tetragonal TiO$_2$ anatase phase [14]. Gradual broadening of the XRD lines, as well as reduction of their intensities, took place with increasing milling time; ultimately, the lines were too broadened and diffused to be identified separately. This feature is clearly shown in Fig. 2, where $d = 0.169$ nm and $d = 0.166$ nm lines of 0 h anatase titania (Fig. 2a) gradually broaden and finally

![Figure 1. Measured surface area and derived particle size of titania versus milling time.](image-url)