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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, α-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 α-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 octahedra 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.

Jamieson and Olinger [5] observed, by X-ray diffraction studies, the direct transition of rutile to the α-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 Bendeliany *et al.* [4] independently reported synthesis of "α-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, α-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 4.33×10^3 to 4.37×10^3 $kg\,m^{-3}$.

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 α-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 α-PbO_2 phase as high as about 90% were obtained from [0 0 1]- 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 % Al_2O_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 $g = 1.994$ situated 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 cretoid 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 5.7×10^3, 8.1×10^3, 10.2×10^3 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 Al_2O_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

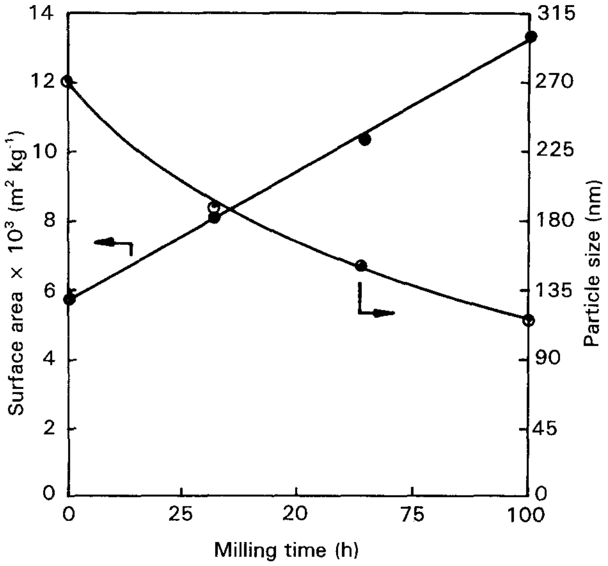

Figure 1 Measured surface area and derived particle size of titania versus milling time.

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

where d is the particle size, ρ is the density of the titania powder ($3.893 \times 10^3\ kg\,m^{-3}$) 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_α line (0.154 178 nm) X-ray source. Slow scan ($1/4°\ min^{-1}$) 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

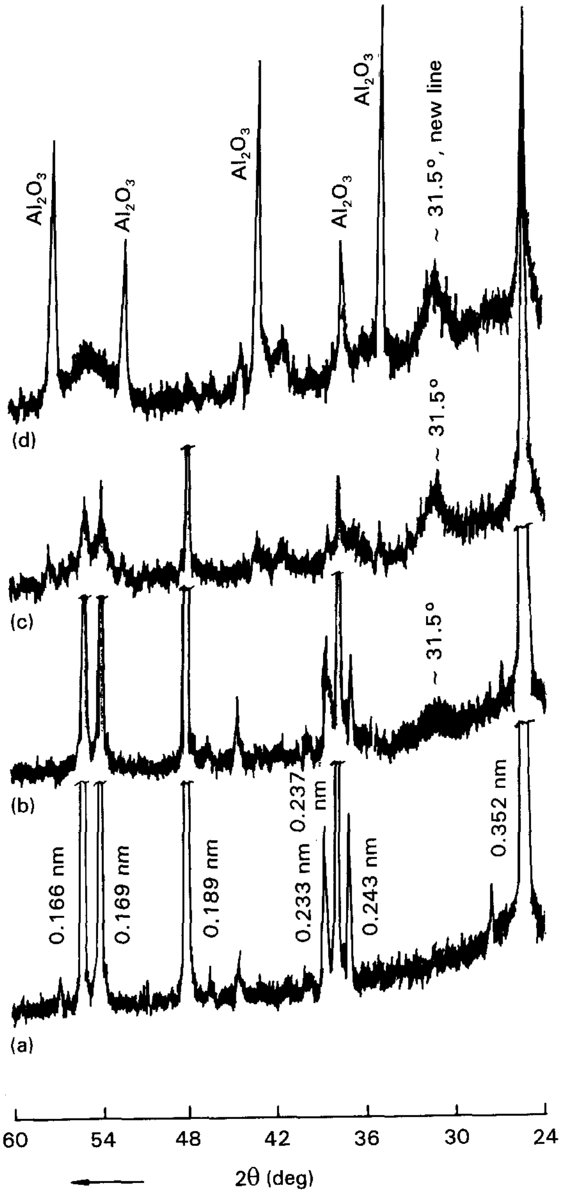

Figure 2 XRD patterns of titania powder ball milled for (a) 0 h, (b) 32 h, (c) 64 h, and (d) 100 h.

merge together to form a diffuse broad band in the 100 h titania sample (Fig. 2d). The appearance of some strong Al_2O_3 diffraction lines in the XRD spectrum (Fig. 2c) of the 64 h milled sample was also observed; these were believed to be contaminants from the alumina container. The XRD spectrum (Fig. 2d) of the sample milled for 100 h showed the same features as of 64 h sample, though the Al_2O_3 peaks were more intense due to greater contamination. In the XRD spectrum (Fig. 2b) of the 32 h milled titania powder, a diffuse broad band centred around $2\theta = 31.5°$ was found to have developed along with the other lines of anatase TiO_2. The XRD spectra (Fig. 2c, d) of higher milling time samples, 64 h and 100 h, confirmed the appearance of a broad band in the system. The observed broad band at $2\theta = 31.5°$ neither corresponds to the diffraction lines of anatase phase titania of the starting material nor to the α-Al_2O_3 phase lines of possible contaminated material from the alumina ball and vial. It is clear from the XRD spectra that the observed band around $2\theta = 31.5°$ is a new phase originating from the anatase phase of titania by HEIVBM. From the XRD spectra it can be said that the new phase developed did not grow further with milling time, but remained within a certain limit. From the estimation of XRD, the phase was measured to be nearly 10–20% of titania anatase. Fig. 3 shows the slow scan and higher sensitivity XRD spectrum of the 64 h milled powder in the range $2\theta = 29$–$39°$; it is clearly discernable that the broad band is highly asymmetric in nature. Although it was very difficult to know the actual number of lines, as well as their peak positions and intensities in the broad band, without deconvolution of the broad band, a tentative idea can be obtained from the shape of the band in the spectrum. Considering the asymmetric nature of the XRD band, the broad band possibly consists of two broad bands, one around $d = 0.285$ nm and the other around $d = 0.275$ nm. There may be some other lines corresponding to the new phase developed whose intensity might be very low, thus preventing detection. From this XRD spectrum it is very difficult to be convinced of the existence of other bands except for these two. The approximate intensity ratio of the two bands is 100:40.

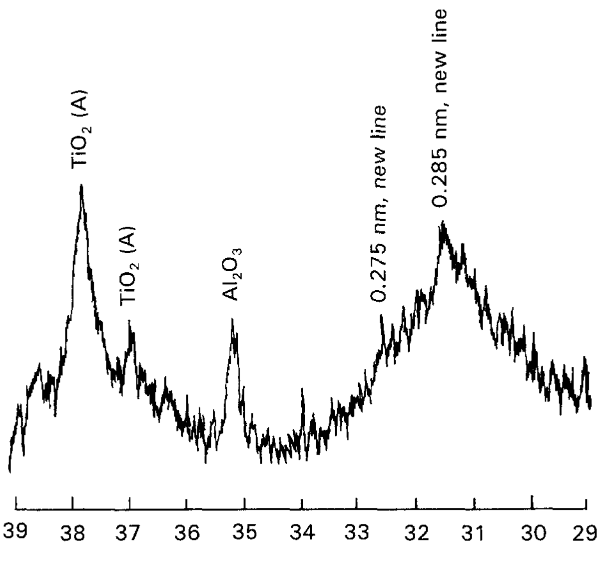

Figure 3 Slow scan XRD pattern of 64 h ball milled titania powder.

3.2. Electron spin resonance

The unmilled titania powder did not show any ESR signal, whereas the powders milled at various times showed ESR signals depending on the length of milling. Three different types of ESR lines in the titania powders milled for various times were observed. The powder milled for 16 h had an ESR line (Fig. 4a) at $g = 1.994$, and the 64 h milled sample showed an ESR line (Fig. 4b) at $g = 1.987$. Whereas, the 100 h milled sample showed an ESR line (Fig. 4c) at $g = 2.008$, along with a weak line at $g = 1.987$.

4. Discussion

The XRD spectrum (Fig. 2a) of the unmilled titania powder showed that the starting material for high

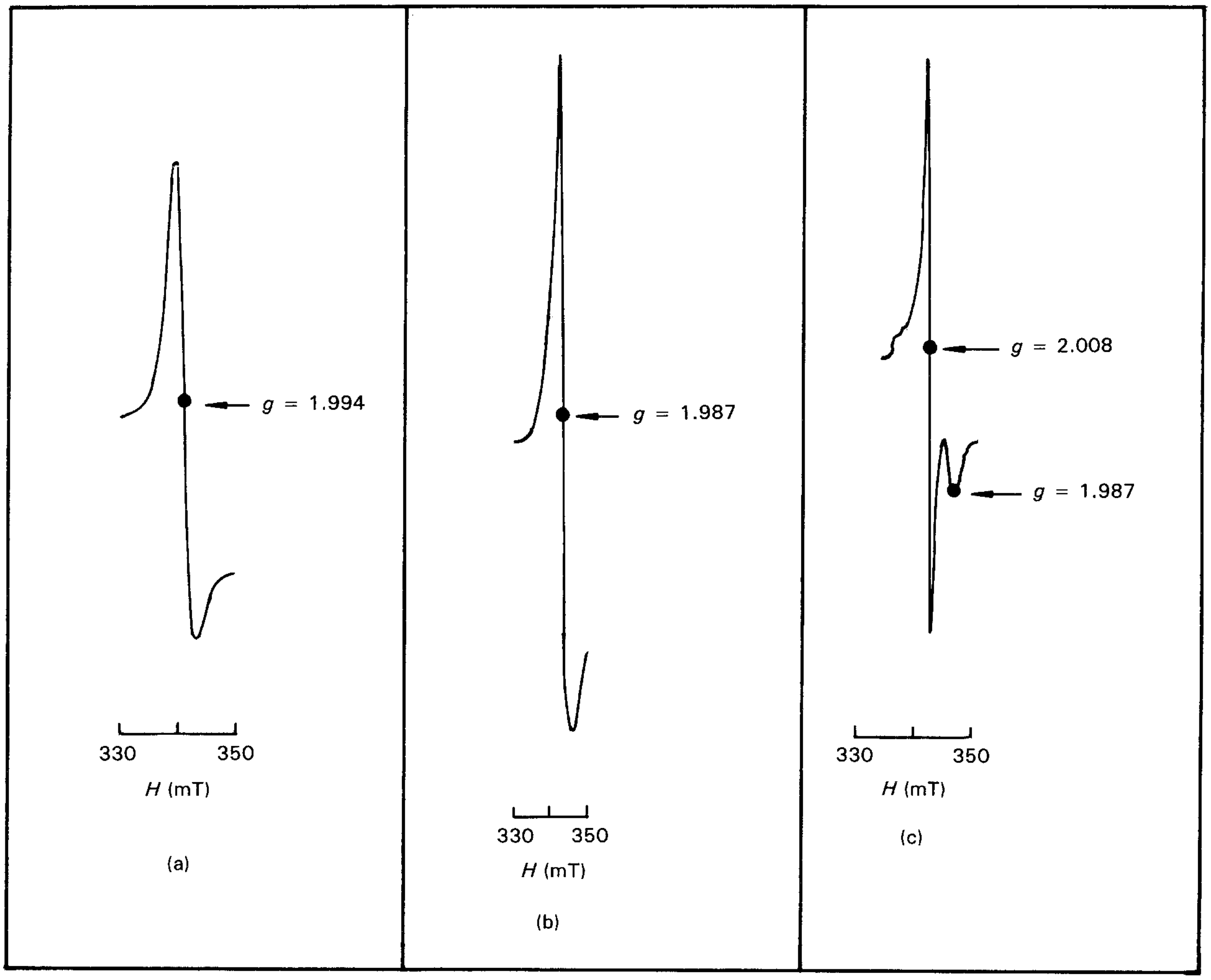

Figure 4 ESR signals of titania powder ball milled for (a) 16 h, (b) 64 h, and (c) 100 h.

energy ball milling was a tetragonal anatase phase belonging to the space group D_{4h}^{19} (I4/amd) [15]. The crystallographic unit cell for this phase contains four TiO_2 molecules for every titanium ion, and is surrounded by six neighbouring oxygen ions, forming a distorted TiO_6 octahedron.

It has recently been shown that ball milling, apart from particle fracture, may induce lattice strain in hard metal carbides and ceramic oxides [8–11]. As TiO_2 is a ceramic oxide, it is highly probable that HEIVBM of the titania powder also results in the introduction of strain in the form of lattice distortion in the material; this is indicated by preferential broadening of the X-ray diffraction lines and by changes in line intensities. Since the vibrational frequency (20 Hz) of the mill is constant, the applied stress on the material also remains constant. The development of strain in the material is constant with time, but the residual strain is additive. Therefore, the cumulative strain which is locked up in the material increases with increasing milling time. The broadening of XRD lines and reduction in line intensities of those titania specimens subjected to lower milling times, Fig. 2, show evidence of increasing strain in the material. The appearance of a new broad band at $2\theta = 31.5°$ in the XRD spectrum (Fig. 2) after 64 h milling confirms the existence of a new phase. The intense band at 0.285 nm in the XRD spectrum of Fig. 3 corresponds to the high pressure (1.5–10 GPa) and temperature (25–500 °C) phase of titania first observed by Dachille and Roy [1] from anatase. The broad nature of the band also confirms the development of a high pressure phase, because the high pressure phase prepared from anatase was always intergrown with a short-range ordered phase which produced broad diffraction peaks [1]. It was also very clear from the reported literature [6, 7] that shock waves are largely responsible for the formation of a high pressure titania phase. HEIVBM used in the present study produces repeated impacts on the powder, which in turn generate impact-shock on the material. The shock wave dissipating through the material leaves behind a quantum of strain in the material, which is cumulative with increased milling time (line broadening). Initially, when the milling time was short a small amount of strain was generated in the material by impact-shock, and much of it was dissipated by particle fracture, as seen by the increased surface area and reduction in particle size (Fig. 1). This amount of strain was not sufficient for polymorphic phase transformation. Probably, it is for this reason that no new line could be identified in the XRD spectra for the lower milling time titania powders. In the case of higher milling times, above 32 h, the amount of cumulative strain generated in the material becomes sufficient, without much loss by particle fracture (Fig. 1), for polymorphic phase transformation of anatase titania to occur. Therefore, it is suggested that when a threshold strain value is reached, the high pressure phase appears. As a result, a new broad band in the XRD spectrum was seen in titania powders milled for more than 32 h. Since the starting material was in powder form, the new phase developed is 10–20% of the bulk titania; which satisfies the 10–30% limit in the case of polycrystalline rutile powder subjected to shock waves [7]. Since the material studied was in powder form, it is probable that only 10–20% of the bulk powder was subjected to impact loading in the mill. The physical reason behind this limit is that the yield of the new phase is highly dependent on the orientation of the crystal with respect to the direction of shock wave propagation. Yields of the α-PbO_2 phase as high as about 90% were obtained by Linde and DeCarli [7] from [0 0 1]- and [1 1 1]-oriented rutile single crystals shocked at 45 GPa, whereas in the case of polycrystalline rutile powder the yield was only 10–30%. The X-ray diffraction lines at 0.285 and 0.275 nm, and the intensity ratio of the two lines, 100:40, highly corroborate with the lines of the reported high pressure phase [orthorhombic α-PbO_2 (Pbcn)] of rutile titania developed by Linde and DeCarli [7]. The line $d = 0.35$ nm, which is the second highest intensity line for the orthorhombic phase, was not found in the developed phase because this line was masked by the highest intensity line, $d = 0.352$ nm, of the anatase phase. From the above data it can be strongly suggested that the observed new phase is a high pressure phase of titania, formed from anatase titania, which has an orthorhombic α-PbO_2 structure after HEIVBM.

The ESR result provides further support for the existence of a high pressure orthorhombic α-PbO_2 phase. The unmilled titania powder did not show any ESR signal, whereas milled titania powders showed sharp ESR signals strongly dependent on the length of milling. Three types of ESR signals were detected from the milled titania powder. Type 1, for the least milled titania powders, e.g. after 16 h, having an ESR line (Fig. 4a) at $g = 1.994$; and type 2, for titania powder milled for longer times, e.g. 64 h, having an ESR line (Fig. 4b) at $g = 1.987$; and type 3, which is titania powder milled for far longer, e.g. 100 h, having an ESR line (Fig. 4c) at $g = 2.008$, along with a weak line at $g = 1.987$.

ESR results of ball milled TiO_2 powder compares well with the results obtained by shocked titania samples observed by Linde and DeCarli [7]. They observed three classes of ESR signals whose "g" values were 1.994, 1.987 and 2.008, respectively, from shocked titania specimens. The three different types of milled titania powders in the present study showed "g" values, 1.994, 1.987 and 2.008, identical to the three different classes of specimens described by Linde and DeCarli [7]. The similarity of the ESR results also confirms that the phase which was developed from anatase titania by HEIVBM has the same orthorhombic α-PbO_2 structure as the high pressure modified form of rutile titania.

5. Conclusions

By analysing the results of XRD and ESR studies it can be concluded that prolonged high energy impact vibrational ball milling creates sufficient impact shock in a localized point, which is very similar to the shock wave generated by dynamic loading, to force anatase titania to grow in a particular fashion, like the orthorhombic α-PbO_2 (Pbcn) structure of the high pressure modified phase of titania. Detailed investigations and calculations are in progress to establish the full structure and the species responsible for the ESR signals of the new polymorph developed.

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