Pressure-induced polyamorphism in TiO$_2$ nanoparticles

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Two different nanometric (6 nm) TiO$_2$ compounds, anatase polycrystals and amorphous particles, were investigated under high pressure using Raman spectroscopy. Nanoanatase undergoes a pressure-induced amorphization. The pressure-induced transformations of this mechanically prepared amorphous state are compared with those of a chemically prepared amorphous particles. In the mechanically prepared amorphous state, a reversible transformation from a low-density amorphous state to high-density amorphous state (HDA1) is observed in the range 13–16 GPa. In the chemically prepared sample, a transformation to a new high-density amorphous state (HDA2) is observed at around 21 GPa. Further compression leads to the transformation HDA2$\rightarrow$HDA1 at $\sim$30 GPa. We demonstrate that depending on the starting amorphous material, the high-pressure polyamorphic transformations may differ. This observation indicates that pressure is a suited tool to discriminate between nanomaterials apparently similar at ambient conditions.

PACS number(s): 64.70.Nd, 61.43.Er, 61.82.Rx

Pressure-induced polyamorphism is an unusual and intriguing phenomenon and many works have been devoted to understanding the underlying mechanisms.[1,2] It consists in a first-order transition between a low-density amorphous state (LDA) and a high-density amorphous state (HDA) through pressure application with significant changes in structure and physical properties of the amorphous solids.[3] Because these polyamorphic transformations are first order, HDA states are potentially quenchable, opening the route to the synthesis of new amorphous materials at ambient conditions. As in their crystalline counterparts, some structures provide interesting properties for potential applications. In the case of amorphous states, it is important to be able to vary some physical properties (for instance, electrical conductivity as in the case of the LDA-HDA transformation in amorphous silicon[3]) associated with intrinsic properties linked to their amorphous nature (mechanical properties or thermal conductivity). However, obtaining a starting amorphous state to generate amorphous-amorphous transformations may be difficult, especially from materials that have remarkable technological applications but are poor glass formers.

Surface effect, when the particle size reaches nanometer, strongly influences the stability of phases. It leads to the observation of new stabilized structures or metastable states. The combination of high pressure and nanometric particle size is an ideal way to obtain metastable amorphous states and to induce polyamorphic transformations. Here, we show that more metastable states than first thought can be obtained by high pressure in TiO$_2$. In addition, we demonstrate that depending on the starting amorphous material, the high-pressure polyamorphic transformations may differ. This observation indicates that pressure is a suited tool to discriminate between nanomaterials apparently similar at ambient conditions.

We used TiO$_2$ as a case study. Titanium dioxide is a particularly attractive and strategic material due to the combination of interesting physical and chemical properties[4] (mechanical, electronic, catalytic, etc.). It has emerged that the combination of size, pressure, and temperature is important to obtain improved physical properties. For instance, the use of extreme conditions of pressure and temperature led to the synthesis of a new phase in TiO$_2$ that appeared to be the hardest oxide discovered up to now.[5] Reducing the size of the particles led to the stabilization of the anatase structure with respect to the rutile one at ambient conditions and in nanosized anatase the phase diagram was strongly modified.[6] First, it was shown that an intermediate high-pressure phase (α-PbO$_2$ columbite) usually observed around 3–4 GPa in bulk TiO$_2$ was suppressed when dealing with nanocrystals.[7] In addition, the transition pressure to the next high-pressure phase is dependent on the particle size.[6] Finally, below a diameter of around 10 nm, a pressure-induced amorphization has been observed.[6–9] The obtained amorphous state has been interpreted as structurally related to the high-pressure monoclinic phase and represents an HDA state.[9] Recent x-ray absorption spectroscopy studies suggest that, depending on the starting experimental conditions, a precursor ordered structure, different from that of anatase, appears before the amorphization.[10] On decompression, a transformation from HDA to LDA state has been observed using Raman spectroscopy and x-ray diffraction.[9] The authors correlate the recovered LDA state to the columbite structure, a crystalline phase usually observed after compression and decompression of the TiO$_2$ crystalline phase. The nature of the recovered LDA phase is still not completely understood. The spectrum at ambient conditions after decompression does not correspond to the Raman spectrum of the amorphous TiO$_2$ that can be obtained by the sol-gel method[11,12] but shows the presence of rather sharp peaks related to the columbite structure, suggesting the presence of some degree of crystallinity in the sample.

The motivation of the present work is to clarify the occurrence of a polyamorphic transformation in TiO$_2$ during the decompression and recompression of a pressure-induced amorphous state, and to compare this with the high-pressure response of an *initially amorphous state*. In this work, we use Raman spectroscopy as it is a powerful technique to investigate the local structure of amorphous compounds and to detect any change in the coordination polyhedra. It revealed polyamorphism in amorphous Si,[3] clathrate,[13] and

several oxides such as SiO_2 and B_2O_3.[14,15] In addition, by comparing the pressure behavior of a mechanically prepared amorphous state (by pressure-induced amorphization of nanocrystals) to a chemically prepared amorphous sample, we emphasize that both particle size and the synthesis route of the amorphous initial state are important factors in pressure-induced polyamorphism.

TiO$_2$ samples were produced using two different synthesis methods. TiO$_2$ nanometric anatase crystals were obtained from TiCl$_4$ by the hydrothermal method as described in Ref. 16 and TiO$_2$ amorphous sample was synthesized by a sol-gel technique as described in Ref. 17. This amorphous state is not stabilized by surface energy as observed in Si (Ref. 18) and predicted by Navrotsky[19] in ZrO$_2$, for instance. The particle size is centered on 6 nm, a size for which the anatase structure is usually observed. However, the formation of amorphous titania instead of single-phase nanoanatase is controlled by the kinetics of the polyhedra rearrangement to attain the anatase structure rather than thermodynamics.[11] Thus, it is possible to obtain metastable amorphous nanoparticles of TiO$_2$ by quenching the reaction during the first minute of the process. Their morphology (spherical) and size (6 nm) were determined by transmission electron microscopy.[14]

Raman spectra of nano-TiO$_2$ were obtained using a customized high-throughput optical system based on Kaiser optical filters and an Acton 300i spectrograph with sensitive charged coupled device detection. Samples were excited using 514.5 nm radiation from an air cooled Ar$^+$ laser. The beam was focused on the sample using a Mitutoyo 50× objective, with beam diameter ~2 μm at the sample. The scattered light was collected in backscattering geometry using the same lens.

In all experiments, high pressure was generated using a membrane diamond-anvil cell with low-fluorescence diamonds. Nanoparticles were placed into a 125 μm chamber drilled in an indented stainless-steel gasket. No pressure-transmitting medium was used during these experiments for the following reasons. First, Swamy *et al.*[6] mentioned that they noticed no difference in the high-pressure behavior of TiO$_2$ nanoparticles when varying the pressure-transmitting medium. Second, nanoparticles have a tendency to strongly aggregate. Using a transmitting medium will not provide hydrostatic compression of all the particles and the intergrain contacts will lead anyway to strong shear stresses even if the medium is still hydrostatic.

Raman spectra of 6 nm crystalline anatase during compression up to ~27 GPa are shown in Fig. 1(a). In agreement with previous work,[6–10] we observed an extended stability range of the anatase structure up to 17.6 GPa. An intermediate phase between the crystalline phase and the amorphous state is observed in a narrow range of pressure and corresponds to the spectrum at 19.4 GPa. The signature of this phase consists of two weak peaks situated at 327 and 374 cm^{-1}. Because of the weakness of the peaks and the coexistence with other features, it is difficult to determine the structure of this phase. The presence of this high pressure stabilized precursor to amorphization has also been reported in a recent x-ray absorption study.[10] However, the nature of this phase seems to depend on the starting experimental con-
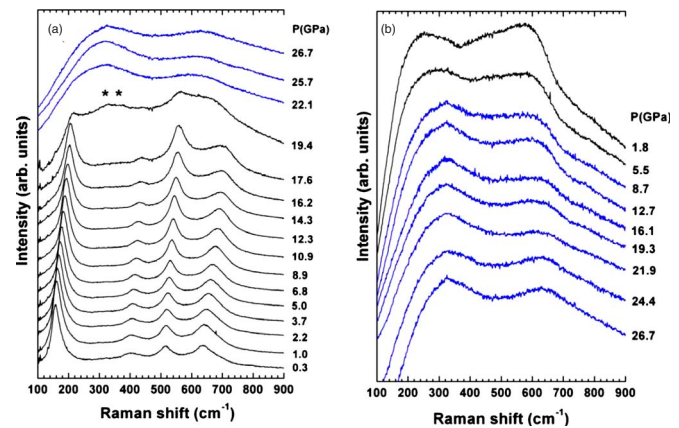

FIG. 1. (Color online) (a) Raman spectra of 6 nm nanoanatase with increasing pressure. Peaks marked with asterisks identified an intermediate state at 19.4 GPa. At higher pressure, broad amorphous bands identified the high-density amorphous state named here HDA1. (b) Raman spectra of the pressure-induced amorphous particles with decreasing pressure. A transformation from the HDA1 to LDA is observed below 5.5 GPa.

ditions and only in some cases has it been identified as the columbite crystalline structure.

The pressure-induced amorphization toward a high-density amorphous state (HDA that we will refer to as HDA1) occurs between 19.4 and 22.1 GPa, in agreement with previous works,[6–10] and is inferred from the appearance of two broad bands at around 320 and 640 cm^{-1}.

On decompression [Fig. 1(b)], no noticeable change is observed in the spectra down to 8.7 GPa. Below 5.5 GPa, the vibrational density of states (vDOS) is modified and indicates that a transformation from an HDA1 state to an LDA state occurs. The spectrum shows three broadbands centered at ~190, ~440, and ~610 cm^{-1}. This spectrum is similar to the known amorphous state of TiO$_2$ obtained by chemical synthesis (Refs. 11 and 12, and Fig. 3). Several studies were undertaken to determine the structure of the LDA state (see Ref. 20 and references therein). It is not clear whether LDA is structure related with anatase or brookite. The most recent study proposes that amorphous TiO$_2$ particles consist of a highly distorted shell and a small strained anataselike crystalline core.[20] The shell contains TiO$_6$ and TiO$_5$ polyhedra with random arrangements. Therefore, the LDA vDOS probably cannot be related to a unique underlying crystalline phase.

This LDA state obtained mechanically after pressure treatment (that we will name p-LDA in the following) has been recompressed up to ~20 GPa (Fig. 2). The transition from the p-LDA state to the HDA1 state is observed between 9.2 and 13.2 GPa and is reversible. These experiments definitively demonstrate that a polyamorphic transformation occurs in pressure-induced amorphized nanoanatase and a clear spectrum of the HDA1 state is presented here. In addition, the high-quality spectra obtained in the present study allowed us to confirm the existence of an intermediate structure in a narrow range of pressure between the crystalline nanoanatase and the high-density amorphous state.

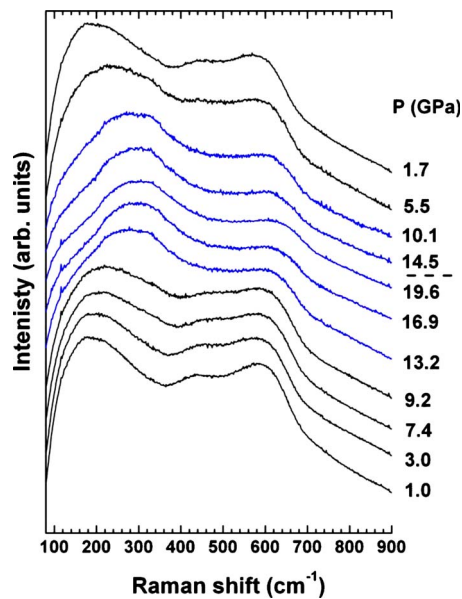We must notice that the Raman spectrum we have ob-

FIG. 2. (Color online) Pressure cycle on an initially LDA state obtained by pressure-induced amorphization of a 6 nm anatase sample (p-LDA) (see Fig. 1). On compression, a transformation from the LDA state to the HDA1 state above 13.2 GPa is observed. The back transformation occurs between 10.1 and 5.5 GPa.
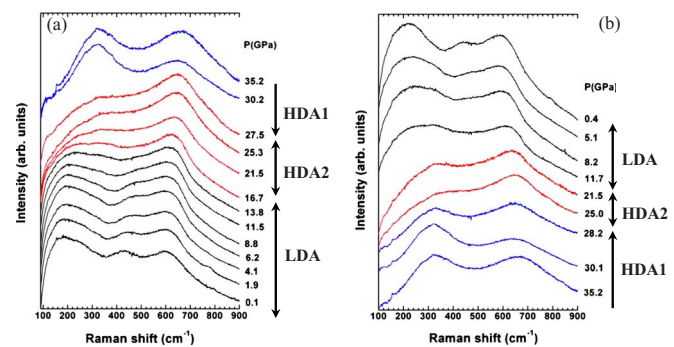

FIG. 3. (Color online) (a) Raman spectra of 6 nm amorphous particles prepared by sol-gel synthesis with increasing pressure. A LDA to a new HDA2 transformation is observed above 16.7 GPa. Above 30.2 GPa, another amorphous state (HDA1) appeared. (b) Raman spectra of 6 nm amorphous particles with decreasing pressure. The back transformation HDA1→HDA2 is observed in the range 28.2–25.0 GPa and the transformation HDA2→LDA starts around 11.7 GPa.

tained for the p-LDA state is not the same as the LDA spectrum obtained after decompression of a pressure amorphized nanoanatase sample of similar size presented in Ref. 9. In that work, four bands are observed at ~180, ~310, ~420, and ~600 cm^{-1}. The three first peaks are much sharper than the ones in our spectra. The authors of Ref. 9 found some similarity between their spectrum of the LDA state and the one of nanocrystalline orthorhombic (columbite) TiO$_2$. They concluded that the LDA form might be structurally related to the columbite phase. Our spectrum of the LDA obtained by the decompression of the pressure-induced amorphous state shows three broad peaks and resembles the one of the amorphous state obtained by the sol-gel synthesis (Fig. 3 and Refs. 11 and 12). The discrepancies between the present work and Ref. 9 may be due to a different sample preparation leading to a change in the surface energy (chemistry factor) or to the shape of the particles. In addition, a partial recrystallization toward the orthorhombic phase may be due to some heating induced by the laser of the Raman system. In Ref. 10, it has been shown that some poorly crystallized orthorhombic phase can be observed after decompression of the pressure-amorphized material.

In the following part, we will detail the results obtained during a high-pressure treatment of the 6 nm amorphous sample synthesized by sol-gel method. The starting material has a spectrum typical of the LDA state of TiO$_2$ as can be seen in Fig. 3(a). The compression of this chemically prepared LDA state (named c-LDA hereafter) does not induce strong changes up to 16.7 GPa. Above this pressure, the bands at 190 and 440 cm^{-1} disappear and the position of the high-wavenumber peak upshifts faster as pressure increases. These evolutions suggest the appearance of a new amorphous state (named HDA2) different from the one obtained

following the amorphization of the nanoanatase structure (Fig. 1). This transition may be related to some rearrangement of the TiO$_6$ octahedra. In the crystalline counterparts, rutile and anatase have different arrangements of the TiO$_6$ units and also show very different Raman spectra, with very low intensity of the low-wavenumber bands in the rutile structure. Such changes in the medium range order of glass under pressure have also been observed in silica.[21] A sudden change in the spectra is observed around 30.2 GPa with the appearance of a strong band centered at 320 cm^{-1}. This spectrum is very similar to the one of HDA1. Thus, we report the appearance of an intermediate density amorphous state (HDA2) between the two previously reported amorphous forms. The following sequence of transformations in the amorphous sample up to 35 GPa: c-LDA→HDA2→HDA1 is observed. Transitions between several amorphous states have already been reported in H$_2$O, where three amorphous states (LDA, HDA, and vHDA) are now well identified, and have been suggested to occur in elemental Si and Ge for which it is not clear yet if the LDA/HDA2 transformation is real, i.e., associated with phase boundary or a continuous change.

On decompression [Fig. 3(b)], a sluggish transformation from HDA1 to HDA2 occurred around 25 GPa. The back transformation to the LDA state is observed around 11.7 GPa. The spectrum of the recovered sample is similar to the one of the starting material indicating a complete reversibility of the pressure-induced transformations.

Figure 4 shows a schematic Gibbs free energy $G(P)$ diagram that can summarize the transformations between the polymorphs of nanometric TiO$_2$ amorphous states. Because $G=U+PV-TS$, the slope is approximately equal to the molar volume (V) at constant T. To account for the different pressure-induced transformations, we assume that the free energy of the two LDA states, prepared either by pressure-induced amorphization (p-LDA) or by the chemical route (c-LDA), are not equal at ambient conditions. As the average diameter (6 nm) and morphology (spheres) are very similar for both starting materials, this difference is probably due to
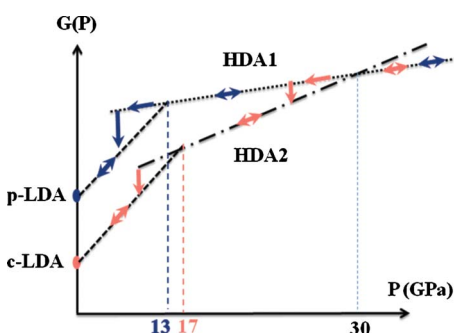
FIG. 4. (Color online) Free energy of different amorphous states as a function of pressure. The red (light gray) arrows indicate the thermodynamic path of the chemically prepared amorphous (c-LDA) on compression and decompression. A reversible c-LDA $\rightarrow$HDA2$\rightarrow$HDA1 transformation is observed under pressure. For the pressure prepared amorphous (p-LDA) [blue (dark gray) arrows] the thermodynamic path is different and no HDA2 is observed.

a different surface chemistry modifying the surface energy or to the presence of defects in the p-LDA generated by pressure treatment. The relative position of the free energy of these LDA states is dictated by the fact that HDA2 is not observed by pressurization of p-LDA.

As pressure is increased c-LDA transforms to HDA2 at $\sim$17 GPa, and the HDA2-HDA1 transition is observed at $\sim$30 GPa. This series of transformation can be represented on the $G(P)$ diagram by the intersection of the different $G(P)$ curves associated to each amorphous state. Strictly speaking, the amorphous solid does not constitute a true phase and equilibrium thermodynamic arguments should not apply. However, thermodynamic quantities such as the specific volume, enthalpy, and entropy are readily measured for solid

amorphous materials and can be used to describe a noncrystalline substance that is in a metastable thermodynamic equilibrium.[22] On decompression, some hysteresis is observed as expected for first-order transformations.

On compression, p-LDA does not transform to HDA2, indicating that the two representative $G(P)$ curves do not cross and that p-LDA must have a higher free energy than c-LDA at ambient pressure. The direct transformation from p-LDA to HDA1 occurs between 9.2 and 13.2 GPa (Fig. 2). On decompression, one may expect a transformation from HDA1 to HDA2, in principle. In practice, this transformation is not observed probably due to kinetic barriers preserving the HDA1 state down to 5.5 GPa, where the p-LDA state appears again.

Our results illustrate the complexity of the transformations between metastable states and the important influence of the initial sample (chemically prepared or mechanically prepared) and of the history of the sample. In addition, despite similar spectroscopic signatures, the initial LDA amorphous states do not show the same high-pressure changes, making the pressure effect an ideal marker to differentiate these samples.

In this study, we have shown that the polyamorphism in nanosized TiO_2 is extremely rich and TiO_2 can now be added to the limited set of compounds known for clearly exhibiting pressure-induced polyamorphism. The variety of amorphous structures is surprising in such a material which is usually considered as a poor glass former. Compared with the bulk, finite-size systems can have richer metastable structures due to the surface effects. The size effect adds a new dimension to the polyamorphism phenomenon and shows that the combination of pressure and ultrafine grain size allows for exploring new energy landscapes.

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