Finite-size and pressure effects on the Raman spectrum of nanocrystalline anatase TiO₂

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The Raman scattering behavior of anatase nanocrystals with average diameters of 4, 8, 20, and 34 nm has been compared with bulk crystal data in order to establish size-dependent changes to the phonon spectrum at ambient conditions. Further, the high-pressure behavior of the anatase nanocrystals was examined at roomtemperature using *in situ* Raman scattering data obtained in diamond-anvil cells to a maximum pressure of 41 GPa. The size-dependent changes to the Raman spectrum are best explained in terms of three-dimensional confinement of phonons in finite-sized nanocrystalline anatase. The difference in slopes obtained for the pressure shifts of Raman modes between nanocrystalline and single crystal anatase is in conformity with the observed size-dependent bulk modulus values. The metastability of anatase as a function of pressure is demonstrated to be size dependent, with smaller crystallites preserving the structure to higher pressures. Three size regimes have been recognized for the pressure-induced phase transition of anatase at room temperature: an anatase-amorphous transition regime at the smallest crystallite sizes, an anatase-baddeleyite transition regime at intermediate crystallite sizes, and an anatase– α -PbO₂ transition regime comprising large nanocrystals to macroscopic single crystals. This size-dependent phase selectivity of anatase at high pressures explains the recent contradictory experimental data. A semiquantitative phase diagram for anatase metastability as a function of size and pressure at room temperature is proposed.

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I. INTRODUCTION

The characterization of finite-size effects on various physical properties and stability of nanocrystalline TiO₂ phases has been the subject of several recent investigations. The interest in nanocrystalline TiO₂ is driven by the immense potential this material, particularly the anatase form, holds for a variety of technological applications. The important technological applications of nanoscale TiO₂ are in photocatalysis, photochemical solar cells, optoelectronic devices, chemical sensors, and dielectric material of ultrathin thin-film capacitors.¹⁻⁴ Nanocrystalline TiO₂ has also played a proven role in fundamental studies of size-induced modifications of physical properties and phase stability in nanoscale inorganic systems.^{5,6} A number of studies have used pressure-induced structural transitions in nanocrystalline chalcogenide semiconductors such as CdS and CdSe as model systems to understand the microscopic mechanisms and kinetics of solid-state phase transitions.⁷ As models of phase transitions, especially size-dependent structural phase transitions, the pressure- and temperature-driven transitions of nanocrystalline TiO_2 have the potential to complement or rival those of the well investigated covalent semiconductor systems such as CdSe, CdS, and Si because of the intrinsic ionicity of the TiO₂ phases and the possibility that finite-size effects can be examined over a wider crystallite size range. Evaluation of size-related changes to the vibrational spectra (Raman and infrared) represents an attractive approach to studies of nanocrystalline TiO₂, for it will not only improve understanding of nanoscale systems, but also assist in practical application of vibrational spectroscopy as a simple and effective tool for the characterization of crystal structure and crystallite size. In this paper, we present a Raman spectroscopic study of the effects of finite-size and high-pressure on nanocrystalline anatase TiO_2 .

Raman spectroscopy is a particularly useful tool to investigate the effects of finite size and high pressure, including pressure-induced amorphization, in semiconductors and insulators.^{8,9} Finite-size effects on the phonon spectra of a variety of materials have been well established by using Raman scattering experiments on nanocrystals in combination with theoretical phonon confinement models.^{8,10–14} In these investigations, the Raman spectral characteristics such as Raman frequencies, line widths, and peak asymmetry have been shown to correlate systematically with crystallite size in materials as diverse as Si, BN, GaAs, CdSe, and AlO(OH). A number of Raman scattering studies have also chosen nanocrystalline TiO₂ in order to characterize the size effects on the Raman spectra and their pressure evolution.^{3,15–19} The changes in the Raman spectrum of nanocrystalline anatase, the phase most commonly synthesized at ambient conditions, have been variously interpreted as originating from phonon confinement,^{15–17,20,21} non-stoichiometry,^{22,23} or internal stress/surface tension effects as observed for similar materials.8,24-26 Although the majority of the published studies have leaned towards phonon confinement as the main factor responsible for the changes observed in the Raman spectrum of nanocrystalline anatase,^{15–17,20,21} some researchers have interpreted their results as favoring one of the other factors. For example, in a study of the size effects on the Raman spectrum of nanocrystalline anatase, the distinct evolution of Raman spectral characteristics of samples annealed

in two different atmospheres, namely air and argon, was ascribed to the influence of Ti:O stoichiometry. The same study, however, obtained calculated frequency shifts for two major Raman bands at 144 and 639 cm⁻¹ (see below) that are consistent with the shifts suggested by phonon confinement effects, but which the authors chose to interpret as reflecting nonstoichiometry effects.³ Establishing the influence of various factors on the Raman spectra of nanoscale TiO₂ phases is essential for exploiting Raman spectroscopy as a sensitive probe to characterize the structure and crystallite size of nanoscale TiO₂.

The effect of pressure on bulk TiO₂ has been investigated extensively using static and dynamic experimental techniques, and a number of pressure-induced structural phase transitions identified. The crystal structures and stability of these phases have been reviewed in our recent paper.²⁷ With the recent discovery of two hard to ultrahard and highly incompressible orthorhombic phases in diamond-anvil cell (DAC) experiments at 28 GPa (Ref. 28) and 61 GPa,²⁹ the pressure-induced phase transitions in bulk TiO₂ at low temperature are well established to about 80 GPa. High-pressure Raman scattering and x-ray diffraction (XRD) studies have established the following structural phase transition sequence for bulk anatase with increasing pressure: columbite (orthorhombic α -PbO₂, space group Pbcn) at 2–12 GPa,^{30–34} baddeleyite (monoclinic ZrO₂, space group $P2_1/c$) at 10–20 GPa (Refs. 32-36) orthorhombic OI (space group Pbca) at 28-38 GPa,²⁸ and cotunnite (orthorhombic PbCl₂ or OII, space group Pnma) above 55 GPa.²⁹

In comparison, there have been relatively few studies of the high-pressure behavior of nanocrystalline TiO₂, with contrasting reports on the high-pressure behavior of nanos-cale anatase and rutile.^{18,19,37-42} Published high-pressure studies of nanocrystalline anatase include a moderate pressure/temperature sintering study³⁸ and room-temperature Raman scattering or powder XRD studies in diamond anvil cells to maximum pressures of 35 to 38 GPa.^{18,19,39-41} Liao and co-workers³⁸ investigated a 96:4 anatase-rutile mixture with an average crystallite diameter of 38 nm in a toroidal type high-pressure apparatus. They reported that depending on the pressure and temperature, the material transformed either to rutile or to srilankite (α -PbO₂ structure). The α -PbO₂ structure formed at pressures greater than 4.75 GPa and temperature as low as 250 °C. At temperatures below about 150 °C, they did not observe the formation of rutile at the expense of anatase up to 8 GPa.

In a Raman scattering study of 7–11 nm sized anatase nanocrystals to 37 GPa,¹⁸ the anatase structure was found to be stable up to 24 GPa, and then turned to a pressurequenchable amorphous phase on further compression in the range of 24–37 GPa. In a subsequent DAC XRD study to 35 GPa of a rutile-anatase mixture (of unknown phase ratio) with average crystallite size of 30 nm,³⁹ the authors suggested that the rutile fraction transformed to the baddeleyite structure at 8.7 GPa while the anatase amorphized directly at 16.4 GPa. Our DAC XRD investigations on a 34 nm anatase to 35 GPa revealed direct transformation of anatase to the baddeleyite structure at 18 GPa without any amorphization.⁴⁰ In addition, the 34 nm anatase showed an enhanced room-temperature bulk modulus in comparison with the bulk phase. An anatase– α -PbO₂ transition, with no hint of amorphization, was observed by Sekiya and co-workers for a single crystal and three powder anatase samples in a DAC XRD and Raman scattering study at room temperature to about 10 GPa.^{41,43} The three powder samples used in this latter study had very large size dispersions (50–500 nm, 1–20 μ m, and 20–100 nm) with unknown mean crystallite size. Towards the completion of this paper, we came across the most recent room temperature, high-pressure DAC Raman study¹⁹ of a non-stoichiometric (TiO_{1.92}) nanocrystalline (~12 nm) anatase, which was reported to transform directly to baddeleyite at 17–18 GPa, similar to the 34 nm anatase in our earlier work.⁴⁰

It is well known that covalent oxides such as SiO₂ polymorphs undergo pressure-induced amorphization (PIA) in the bulk while there have been no report of PIA in bulk TiO_2 . In order to further investigate the effect of size in PIA of anatase TiO_2 we compare the high-pressure behavior of bulk anatase with four nanocrystalline samples representing a spread of average crystallite size. We first revisit the details of the Raman spectrum of nanocrystalline anatase at ambient conditions by examining experimental data obtained on our samples together with data from literature and comparing these with theoretical model predictions. Unlike previous studies, we use well characterized samples prepared using different synthesis methods so that compositional influences on the Raman spectrum are kept to a minimum. Next, we examine the effect of pressure on the Raman modes across the size range by evaluating in situ high-pressure Raman data obtained in DACs to 30-41 GPa. The pressure stability of the anatase structure at room temperature will be examined as a function of average crystallite size. This will help reconcile the published contradictory results on the highpressure behavior of anatase: pressure-induced amorphization versus crystal-crystal structural phase transitions. The theoretical background of the three-dimensional phonon confinement model used to describing nanoscale systems is briefly reviewed below.

II. THE PHONON CONFINEMENT MODEL

The phonon confinement model (also referred to as spatial correlation model or q vector relaxation model) links q vector selection rule for the excitation of Raman active optical phonons with long-range order and crystallite size.^{8,10,12,13,15} In a perfect "infinite" crystal, conservation of phonon momentum requires that in first-order Raman scattering only optic phonons near the Brillouin zone (BZ) center ($q \approx 0$) are involved. In an amorphous material, on the other hand, owing to the lack of long-range order, the q-vector selection rule breaks down and the Raman spectrum resembles the phonon density of states. Nanocrystals represent an intermediate behavior. For a nanocrystal of average diameter L, the strict "infinite" crystal selection rule is replaced by a relaxed version, with the result that a range of q vectors (as large as $\Delta q \approx 1/L$) is accessible due to the uncertainty principle.^{8,15}

In this paper, we use the q vector relaxation model¹⁵ (QVRM) for the purpose of comparing experimental data with theoretically predicted phonon confinement behavior in

anatase nanocrystals. According to this model, for finite sized crystals, the Raman intensity can be expressed using the relation:^{8,10,15}

$$I(\omega) \propto \int dL \rho(L) \int_{BZ} \exp(-q^2 L^2/8) \frac{d^3 q}{[\omega - \omega(\vec{q})]^2 + [\Gamma_0/2]^2},$$
(1)

where $\rho(L)$ is the particle size distribution, q is expressed in units of π/a_L (a_L is the unit cell parameter), $\omega(\vec{q})$ is the phonon dispersion, and Γ_0 is the intrinsic linewidth of the bulk crystal. A spherically symmetric phonon dispersion curve [Eq. (1)] is assumed and approximated by a simple linear chain model.^{12,15} For a given phonon mode, the slope of dispersion away from the BZ center determines the nature of the modification in the Raman line shape as a function of crystallite size: a negative slope, towards lower frequency, would produce a downshifted (redshifted) Raman peak, while a positive slope would result in an upshifted (blueshifted) Raman peak, in addition to an asymmetric peak broadening, as the crystallite size reduces. The most intense E_{σ} Raman mode at 144 cm⁻¹ for bulk anatase is commonly chosen for analysis. The phonon dispersion relations of anatase are not known experimentally owing to the lack of measured inelastic neutron scattering data. In order to overcome this, the experimentally known phonon dispersion relation of the 142 cm⁻¹ B_{1g} mode of rutile, which is the nearest in frequency to that of the 144 cm⁻¹ mode of anatase, has been used successfully as a proxy in the modeling efforts.^{3,15}

III. EXPERIMENTAL DETAILS

A. Nanocrystalline samples

Four nanocrystalline anatase samples, designated A, B, C, and D, were used in this study. They are high-purity (>99% TiO₂), single phase white powders synthesized using different methods. Sample A was prepared using the "sol method"⁴⁴ starting with TiCl₄. Poor dispersion of the crystallites prevented determination of the size distribution using transmission electron microscopy (TEM). With powder XRD the as-prepared material was characterized as anatase with slightly poor crystallinity (in relation to normally heattreated anatase), and using the Scherrer equation we estimated an average crystallite size of 4 ± 1 nm. The unit cell parameters obtained are a=3.806(2) Å and c=9.481(26) Å.

Sample B was obtained from a commercial supplier sample G-5 of Millenium Chemicals.⁴⁵ It was prepared through sulphation of ilmenite (FeTiO₃) and subsequent filtration, neutralization, washing, and spray-drying. The unit cell parameters obtained from powder XRD are a=3.7953(7) Å and c=9.5098(65) Å. An average crystallite size obtained from XRD data using the Scherrer equation is 8±2 nm (poor dispersion did not allow a TEM size determination for this sample also).

Sample C was prepared using a template method⁴⁶ where agarose gel was used as the templating material. The gel was soaked in titanium isopropoxide (70 wt. %) stock solution which was then hydrolyzed and condensed, dried at room

temperature, and finally annealed at a maximum temperature of 450 °C. The anatase crystallites with unit cell parameters of a=3.7864(3) Å and c=9.5051(17) Å gave an average size of 24.4 nm with the powder XRD (Scherrer) method. Analysis of TEM images, however, showed a larger dispersion, with a predominant size distribution in the 12–34 nm range and a very small fraction (<1%) of the crystallites lying outside this range. We estimate the predominant size fraction to be in the range of 20 ± 8 nm.

Sample D was obtained from a commercial supplier. It was prepared using what is termed "Altair process".⁴⁷ The sample consists of equiaxial crystallites with an average diameter of 34 nm (as determined by the supplier with the Scherrer, BET, and TEM methods). Although majority of the crystallites fall near 34 nm, we estimated a narrow crystallite size distribution in the range of 30–40 nm from TEM data and an average size of 32 ± 5 nm based on Williamson-Hall plot⁴⁸ of powder XRD data. The measured unit cell parameters are a=3.7878(5) Å and c=9.5125(24) Å.

B. Raman spectroscopy

The Raman scattering measurements were carried out on a Dilor XY system with the 514.5 nm Ar^+ ion laser as the excitation light. The scattered light was collected in the backscattering geometry using a liquid nitrogen cooled CCD detector. The incident laser power was 50-75 mW for the measurements in air, while for samples inside the DAC (see below) the power varied in the range 100-200 mW. No modifications in the Raman peaks were noticed within the laser power range used in our experiments. The spectrometer was calibrated using the Γ_{25} phonon of diamond Si (Fd -3m). The peaks were analyzed using the PeakFitTM program by Jandel Scientific. The Savitsky-Golay data-smoothing algorithm⁴⁹ was used in the peak analysis. Combinations of Lorentzian and Guassian functions were used to describe the peak profile. We estimate a resolution of 1 cm⁻¹ for the Raman peak position and 0.5 cm⁻¹ for the peak width [full width at half maximum (FWHM)] at ambient conditions.

C. High-pressure Raman spectra

High-pressure, room temperature Raman spectra were obtained using the DAC technique. We used type Ia diamonds in four- and three-pin type DACs.⁵⁰ The sample was placed without any pressure-transmitting medium in a 150 μ m preindented hole of a stainless steel gasket and a tiny (~3 μ m in diameter) ruby sphere chip positioned near the center of the hole. The sample pressures were determined from the pressure dependent shift of the ruby fluorescence R_1 line.⁵¹ The pressure-induced frequency shifts were monitored to about 40 GPa and then the DAC was gradually decompressed to ambient pressure. Previous studies^{18,29,39,40} have established that the absence of a pressure-transmitting medium does not affect the high-pressure behavior of TiO₂ significantly in the pressure range of this study.

IV. RESULTS AND DISCUSSION

A. Raman spectra at ambient conditions

The anatase crystal structure is tetragonal (space group $I4_1/amd$) with two TiO₂ units in the primitive cell, giving



FIG. 1. Ambient pressure Raman spectrum of anatase with average crystallite size of 4 ± 1 nm (A), 8 ± 2 nm (B), 20 ± 8 nm (C), and 34 ± 5 nm (D). The spectrum marked "E" is from a bulk (micrometer-sized) anatase. The symmetry assignments^{52,53} are also marked for the Raman modes.

six Raman-active fundamentals in the vibrational spectrum: three $E_{\rm g}$ modes centered around 144, 197, and 639 cm⁻¹ (designated here $E_{g(1)}$, $E_{g(2)}$, and $E_{g(3)}$, respectively), two B_{1g} modes at 399 and 519 cm⁻¹ (designated $B_{1g(1)}$ and $B_{1g(2)}$), and an A_{1g} mode at 513 cm⁻¹.^{52,53} The symmetry assignment of the 513 and 519 cm⁻¹ modes has been difficult because of the overlap the two modes in experimental Raman spectrum (these modes were resolved only in low temperature measurements) and reversed frequency order obtained in some of the lattice dynamic and first-principles calculations.⁵⁴ In Fig. 1 we present the room temperature Raman spectra of the four nanocrystalline samples along with that of a commercial bulk (micrometer-sized) anatase. As anticipated, increased broadening and systematic frequency shifts of the Raman peaks are seen when going from the bulk to finer-grained samples. The most intense $E_{g(1)}$ mode shows the maximum blueshift and significant broadening among the nanocrystalline samples, both effects increasing with decreasing crystallite size. A small blueshift is seen for the $E_{g(2)}$ mode, while the $B_{1g(1)}$ mode and the $B_{1g(2)}+A_{1g}$ modes show very small blueshifts and red shifts (the latter peak represents a combined effect of two individual modes), respectively. Whereas the frequency shifts for the A_{1g} and B_{1g} modes are not pronounced, increased broadening with decreasing crystallite



size is clearly seen for these modes also. The $E_{g(3)}$ mode shows significant broadening and a redshift with decreasing crystallite size.

A correlation between Raman frequency and peak width has been established as a characteristic feature of the Raman spectra of nanocrystalline materials.^{10–14} In Fig. 2 data on peak position versus line width (FWHM) for the $E_{g(1)}$ mode obtained on our samples as well as from literature are presented. A linear correlation is clearly seen for the Raman frequency–peak width data. It must be mentioned that the two outlying samples from Ref. 21 with the largest peak widths contained a significant fraction of rutile, and this might have influenced the measured Raman shift and FWHM. Similarly, the datum on the ~12 nm anatase from Ref. 19 (asterisk in Fig. 2) represents a nonstoichiometric composition (TiO_{1.92}) and, therefore, will be disregarded from further comparisons below.

In Fig. 3 the $E_{g(1)}$ peak positions (a) and peak widths (b) of our samples are plotted against crystallite size along with other data from the literature. Also shown is the QVRM curve.¹⁵ The agreement between the experimental data and the model is good given that the model involves some assumptions and that the phonon dispersion used to calibrate the model is that of rutile, not anatase. If the data from Ref. 3 are disregarded, a much better agreement is obtained be-

FIG. 2. Raman peak position–linewidth (FWHM) correlation for the $E_{g(1)}$ mode. A (large hollow triangle), B (large hollow diamond), C (large hollow circle), D (large hollow square), and E (large filled square) are the samples shown in Fig. 1. The literature data: filled diamonds (Ref. 15), small hollow squares (Ref. 17), filled triangles (Ref. 20), filled circles (Ref. 21), and asterisk (Ref. 19).



FIG. 3. The Raman frequency (a) and linewidth (FWHM) (b) of the $E_{g(1)}$ mode versus crystallite size. The sources of the data: samples A–E from this study (see Fig. 2); small hollow squares (Ref. 17); filled diamonds (Ref. 15); filled triangles (Ref. 20), crosses and pluses represent air-annealed nanocrystalline anatase synthesized with different relative water concentration during solgel hydrolysis (Ref. 3), and small hollow circles (Ref. 16). The curve is according to the QVRM model (Ref. 15). (c) Raman peak width (FWHM) versus crystallite size for the $B_{1g(1)}$ (hollow squares), $A_{1g}+B_{1g(2)}$ (hollow triangles), and $E_{g(3)}$ (hollow diamonds) modes obtained for samples A–E. The curve is shown only as a guide to the eye, but has remarkable similarity to the QVRM curve shown in (a) and (b).

tween the experiment and QVRM for FWHM versus crystallite size. The Raman peak positions are known to show scatter among different experiments. Because of the better reliability of the peak width as an indicator of the crystallite size, in Fig. 3(c), we present the FWHMs of the other three major Raman peaks against crystallite size for our samples. A curve drawn through the data shows very similar behavior to the one predicted by the QVRM for the $E_{\sigma(1)}$ mode.

The good agreement obtained between the experimental Raman data and the phonon confinement model predictions suggests that spatial confinement of phonons in finite-sized nanocrystals is the major factor determining the Raman spectral characteristics of nanocrystalline anatase. As it has already been demonstrated, surface tension and internal stress are not major factors influencing changes in the anatase Raman spectrum.^{22,23} (We will describe the effect of hydrostatic pressure below.) Nonstoichiometry can be a significant factor contributing to the changes in the Raman spectrum of anatase nanocrystals.^{22,23} Oxygen-deficiency is the most common form of nonstoichiometry in TiO₂, though substitution of oxygen by other radicals can also result in offstoichiometry. Nonstoichiometry as the single major factor affecting the Raman spectral characteristics of our nanocrystalline samples can be ruled out on the following grounds. oxygen-deficient samples normally First. are blue-colored^{22,23,55} whereas our samples are opaque white (fully oxidized). In this study, we deliberately chose samples prepared by a variety of methods so that systematic composition dependence can be avoided (unlike in other studies where samples prepared by a specific method were coarsened subsequently by thermal annealing to obtain the required size range with the possibility of propagating any compositional influence across the size range). The preparation methods of our samples (see Experimental Details) do not involve uncontrolled oxidation of Ti that could result in nonuniform conversion to TiO₂.^{22,23} The possibility of residual reactant species left in the samples is also not high, especially for the thermally annealed samples (B–D), for annealing normally removes these species. We concede that the Raman characteristics of sample A may be marginally affected by synthesis effects because it was used as-prepared without subjecting to high enough temperatures to remove all the residual sol (suggested by the poor crystallinity) and other species. However, as we show below, the data obtained on this sample also conform to the general trends shown by other samples.

We should mention here in passing that the calibration of nonstoichiometry effect against Raman spectral characteristics of the nanocrystalline anatase carried out in the earlier work^{22,23} was complicated by a number of factors: spatial inhomogeneity in the samples and consequent visual separation of "colored" regions; the presence of rutile in addition to anatase; pressure compaction of the as-prepared clusters; and possible grain growth and variable growth and phase transition kinetics during postcondensation heat treatments in air and argon atmospheres. It should also be mentioned that on the basis of data obtained on thin film samples prepared by more homogeneous oxidation of Ti from gas phase condensation (produced by a pulsed microplasma cluster source), it has been concluded that only phonon confinement effects related to cluster dimensions are responsible for observed Raman spectral modifications of nanocrystalline anatase.²¹ The samples in this latter study did not suffer from any thermal annealing or postdeposition treatment.



FIG. 4. Pressure dependence of the anatase Raman modes: (a) $E_{g(1)}$ mode, (b) $B_{1g(1)}$ mode, (c) $A_{1g}+B_{1g(2)}$ modes, and (d) $E_{g(3)}$ mode. The symbols used are as follow: hollow triangles-sample A; hollow diamonds—sample B; hollow circles—sample C; hollow squares—sample D; filled circles—7-11 nm anatase (Ref. 18); filled squares—single crystal (Ref. 33); and small filled diamonds—single crystal (Ref. 43).

B. The pressure dependence of Raman modes

In Fig. 4 we have compiled the pressure dependence of the major anatase Raman modes obtained in this study along with data from the literature on a 7–11 nm anatase¹⁸ and bulk anatase.^{33,43} The "powder" data from Ref. 41 are not useful for our purpose of obtaining size-dependent trends because the data presumably represent the average of three samples that have very large crystallite size dispersions. The $E_{g(2)}$ mode is important from the point of pressure-induced phase transition on account of the suggested mode softening

behavior.^{43,56} This mode is too weak under pressure for the nanocrystalline samples of this study to determine its pressure dependence. Although measurements were carried out to 30–41 GPa for individual nanocrystalline samples, the pressure data presented in Fig. 4 show only the Raman peaks that could be resolved with least errors in the data analysis. It is clear that the pressure dependence of the Raman modes obtained in this study are all well represented by linear increases in Raman shift with pressure. However, zooming in at the low pressure end (Fig. 5), a small dip (minimum) in



FIG. 5. Pressure dependence of the $E_{g(1)}$ mode (samples B and C) showing a minimum at low pressures.

the pressure versus Raman frequency data for $E_{g(1)}$ is apparent near 1 GPa for the nanocrystalline samples. A similar minimum, albeit at a slightly higher pressure, for the $E_{g(1)}$ pressure-linewidth data was observed for the ~ 12 nm anatase, and was explained as due to external applied pressure compensating for the internal pressure (at the minimum) in the nanocrystal.¹⁹

The strongest anatase mode, $E_{g(1)}$, shown in Fig. 4(a) can be traced unambiguously to high pressures (above 20 GPa, depending on the crystallite size) in the nanocrystalline samples, despite the effects of peak broadening, intensity decrease, and phase transitions (see below). It is clear that the use of Ti³⁺:sapphire laser to suppress the fluorescence effect of diamonds in the DAC has compromised the quality of the Raman spectra obtained by Wang and Saxena¹⁸ at the low wave numbers where the plasma effect from laser is very significant. Wang and Saxena¹⁸ suggested that the observed blue shift of the $E_{g(1)}$ mode is likely caused by laser heating and plasma effect. Heating effects should normally move the mode to lower, not higher, wavenumbers. Interestingly, this mode was shown to exhibit unusual hardening behavior (shift to high wave numbers) with enhanced temperature.¹⁹ In spite of this observation, the heating effect of the laser (at low powers) is not expected to alter the peak position to the degree phonon confinement does. The positive shift of the Raman modes at high pressures places the $E_{g(1)}$ mode away from the region where the plasma effects are dominant, and at such pressures the Wang-Saxena¹⁸ data give a slope and blueshift that are consistent with other data. It is interesting to note that with the exception of the two low-pressure points at 0.1 and 1.04 GPa the pressure dependence of the $E_{g(1)}$ mode in bulk anatase from Ref. 33 can also be described by a linear relationship with a slope very similar to that given by our nanocrystals. The single crystal data of Sekiya and co-workers⁴³ give a slightly steeper slope. Overall, the pressure dependence of the $E_{g(1)}$ mode across the size range is similar and the size-dependent blueshift is maintained, beginning with the ambient pressure spectrum.

The other modes shown in Figs. 4(b)-4(d) also display linear pressure dependence. Within the scatter of the individual data set, these modes also do not show significant change in the slope across the nanocrystalline samples. A small divergence is seen for the $B_{1g(1)}$ mode [Fig. 4(b)] of the nanocrystalline samples that suggests a size-dependent change in the pressure dependence. The pressure shifts of the Raman frequencies obtained for our nanocrystalline samples are consistent with the size-dependent blueshifts or redshifts seen for the spectrum at ambient conditions. The pressure dependence of the Raman modes reported for single crystals in two separate studies^{33,43} have slightly steeper slopes in relation to those of the nanocrystals and these data do not show consistent size-related frequency shifts. The intensities of these Raman peaks are much weaker under pressure (compared to that of the $E_{g(1)}$ peak) and the peak position measurements will, therefore, have more associated imprecision.

The different slopes observed for the pressure dependence of nanocrystalline and single crystal anatase Raman modes reflect different size-related compression behavior. The shallower slopes of the nanocrystal modes are in conformity with

TABLE I. Raman frequencies and ambient-pressure isothermal mode-Grüneisen parameters (γ_{iT}) for bulk and nanocrystalline anatase TiO₂. The γ_{iT} 's were calculated assuming linear pressure dependence of Raman modes.

Mode (cm ⁻¹)	Symmetry	Bulk (Ref. 33)	Bulk (Ref. 43)	Sample D
144	E_{g}	3.74	3.97	4.23
399	B_{1g}	1.25	1.41	1.58
518	$A_{1g} + B_{1g}$	0.69	1.05	1.08
639	E_{g}	1.10	1.10	1.08

the enhanced bulk modulus values.^{34,40,57} The isothermal mode-Grüneisen parameter, γ_{iT} , is an important thermody-namic parameter, defined as⁵⁸

$$\gamma_{iT} = \frac{K_T}{v_i} \left(\frac{\partial v_i}{\partial P} \right)_T,\tag{2}$$

where v_i is the vibrational frequency, K_T isothermal bulk modulus, P pressure, and T temperature. We present in Table I the calculated ambient pressure γ_{iT} values for the two bulk^{33,43} and a nanocrystalline anatase (sample D) using the available isothermal bulk modulus data.^{34,40,57} Notwithstanding the scatter of the pressure dependence data, it is clear that a size dependence is seen for the γ_{iT} values. This is especially clear for the most intense $E_{\rm g}$ modes at 144 and 639 cm⁻¹ (the data for bulk anatase $E_{g(1)}$ mode from Ref. 33 admittedly has a slight curvature). The size-dependent γ_{iT} values imply size-dependent anharmonic contributions to the thermodynamic properties of anatase. Available calorimetric data on isobaric heat capacity of 16 nm, 26 nm, and bulk anatase clearly show size-dependent variation of this thermodynamic function.⁵⁹ The isobaric (C_p) and isochoric heat capacities (C_n) are related as⁶⁰

$$C_p - C_v = VT\beta^2 K_T,\tag{3}$$

where *V* is volume and β the coefficient of volume thermal expansion. Thus the quantity on the right-hand side, which essentially represents the anharmonic contribution, must be size dependent. Size-dependent compression behavior, reflected in the pressure shifts of Raman modes discussed above and observed in our earlier DAC XRD study⁴⁰ (contrary to the opposite suggestion^{18,19}), is definitely a contributing factor for the size-dependent anharmonicity, as is possible size-dependent phonon-phonon interactions at elevated temperatures.¹⁹

C. Size-dependent metastability and phase transition of anatase

In order to examine the effect of crystallite size on the structural stability of anatase, we have followed the pressure evolution of the Raman spectra, specifically that of the strongest $E_{g(1)}$ band, of all the four nanocrystalline anatase to pressures of 30–41 GPa. Depending on the average crystallite size, two distinct pressure evolution trends were observed for the nanocrystalline samples (Fig. 6). The $E_{g(1)}$





peak of sample A became progressively broader and weaker with pressure, and by about 21 GPa only a broad feature remained with a large background characteristic of disordered (amorphous) material [Fig. 6(a)]. Further compression to 41 GPa did not produce any major change in the spectra, only progressive weakening and broadening of the peaks. An amorphous phase was recovered upon decompression to ambient pressure. Owing to the better crystallinity of sample B, its $E_{g(1)}$ peak could be followed to about 26 GPa, despite progressive broadening and intensity reduction. At about 26 GPa the Raman spectrum became that of an amorphous phase [Fig. 6(a)]. We further compressed the sample to 32 GPa without noticing any significant change in the Raman spectrum. The sample recovered at room pressure was also amorphous.

The compression behavior of sample C is distinctly different. In this case, all the four major anatase Raman peaks were traceable to about 15 GPa, and close to 16 GPa new peaks corresponding to baddeleyite appeared in the Raman spectrum [Fig. 6(b)]. Upon further compression in the range 16–39.1 GPa, the intensity of the baddelevite peaks progressively dropped and the spectrum evolved into a featureless one. The sample decompressed to room pressure transformed to the α -PbO₂ structure without any noticeable residual amorphous component. Essentially similar compression behavior was shown by sample D also. For this sample, the suggestion of a new phase was already apparent by 11.3 GPa in the predominantly anatase Raman spectrum [Fig. 6(b)]. Distinct baddeleyite peaks appeared by about 15 GPa. Anatase and baddeleyite peaks were present in the Raman spectra recorded over a wide pressure range, with the peaks from the latter growing steadily to 25 GPa. The baddeleyite peaks became weaker with further compression, but we did not observe complete amorphization (although an increased background is seen at high pressures) up to 30 GPa. On decompression to about 8 GPa, the peaks of baddeleyite became progressively better defined, and by about 4 GPa the Raman spectrum had both baddeleyite and α -PbO₂ peaks



FIG. 7. Semiquantitative phase diagram showing sizedependent metastability of anatase with pressure. The data shown: hollow circles (samples A–D of this study), filled square (Ref. 18), filled triangle (Ref. 39), and filled diamond (Ref. 19). The curve, fitted to available data, represents approximate metastability limit of anatase.

superimposed. The sample recovered at room pressure contained only α -PbO₂. A comparison of the high-pressure Raman results on sample D with corresponding XRD data⁴⁰ suggests an overall similarity between the two sets of data, however, with an important difference: the onset of phase transition is detected at a lower pressure in the Raman spectra, suggesting a higher sensitivity of the technique to identifying pressure-induced structural phase transformations.

In Fig. 7 the onset pressure of phase transition of anatase nanocrystals obtained in this study as well as in other studies^{18,19,39} is presented as a function of crystallite size. Sample A from our study falls slightly off the phase transition pressure trend suggested by other data. This is most probably due to the comparatively poor crystallinity of sample A. In order to be consistent with the size-dependent phase transition behavior, the datum from Ref. 39, represented by solid triangle, should belong to an anatasebaddeleyite transition, not anatase-amorphous transformation as reported. In fact, from the high-pressure XRD data presented in Fig. 2 of Ref. 39, there appears to be an enhancement in the intensities of the baddelevite peaks at the expense anatase peaks at 16.4 GPa and beyond (compare the intensities of baddelevite peaks in the XRD spectra obtained at 8.7, 12.9, and 16.4 GPa). This suggests that the anatase nanocrystals had indeed transformed to baddeleyite at 16.4 GPa, not to an amorphous phase as concluded by Wang and co-workers.³⁹ The anatase-baddeleyite transition point for the \sim 12 nm TiO_{1.92} anatase also falls slightly away from the trend suggested by other samples, reflecting most likely the compositional difference.

In our earlier paper⁴⁰ we hypothesized on the possibility of a "critical size" required for PIA of nanocrystalline anatase. This possibility is actually borne out by the data shown in Fig. 7. It is possible to recognize three crystallite size regimes with regard to pressure-induced phase transitions of anatase at room temperature in Fig. 7. In the first regime, the application of pressure transforms anatase to an amorphous phase at relatively high pressures (greater than about 20 GPa). This regime approximately overlaps the crystallite size range where phonon confinement effects are most pronounced (to about 12 nm). The second intermediate regime covers the size range where PIA is replaced by direct conversion of anatase to baddeleyite upon compression to moderate pressures. The lower end of this regime approximately coincides with the saturation of the phonon confinement effect while the upper end marks the direct conversion of anatase to α -PbO₂. The third "bulklike" regime comprises the large nanocrystals⁴¹ size range of through microparticles^{19,32,34} to single crystals,^{33,34,43,61} where direct anatase- α -PbO₂ transition is easily achieved in highpressure experiments around 5 GPa. The phase relations shown in Fig. 7 are only qualitative, or at best semiquantitative. We are presently investigating the limiting critical sizes of these three size regimes to arrive at a more quantitative metastability diagram for anatase.

V. CONCLUSIONS

By combining experimental Raman scattering data on well characterized nanocrystalline anatase samples of average crystallite size 4, 8, 20, and 34 nm with literature data and comparing these with theoretical phonon confinement model predictions, we have shown that the changes in the Raman spectral characteristics (Raman shift and linewidth) can be described as the result of spatial confinement of phonons in finite-sized nanocrystals. We have used in our analysis stoichiometric anatase nanocrystals with a size range extended to smaller crystallite sizes than investigated in earlier analyses to establish that phonon confinement, not nonstoichiometry or stress effects, as the most plausible reason for size-induced changes in the Raman spectrum.

In situ high-pressure Raman scattering data obtained in diamond anvil cells at room-temperature were used to examine the effects of hydrostatic pressure on the Raman spectrum of the nanocrystalline anatase. Similar to bulk anatase, the major Raman modes in the nanocrystalline samples also show linear pressure shifts. However, the Raman modes of bulk and nanocrystalline samples show different slopes for

the pressure shifts. The shallower slopes observed for the nanocrystal Raman modes are in accordance with their sizeeffected enhanced bulk modulus. The distinct pressure evolution of the nanocrystals suggests on the one hand enhanced pressure stability of the anatase structure at the nanoscale, and on the other, a size-dependent phase transition behavior. The anatase nanocrystals with smaller average crystallite sizes underwent pressure-induced amorphization, as previously observed,¹⁸ whereas the coarser nanocrystals transformed directly to baddelevite under pressure. A consolidation of the available data suggests that three crystallite size regimes exist with regard to pressure-induced phase transitions of anatase at room temperature: the first regime is characterized by the pressure-induced amorphization of nanocrystals typically less than about 12 nm; in the second regime (size range $\sim 12-50$ nm) anatase transforms directly to the baddeleyite structure; and in the third regime (crystal sizes \geq 40–50 nm) anatase transforms directly to the thermodynamically stable α -PbO₂ structure. Thus, our work establishes size-dependent phase selectivity of pressure-induced phase transitions in anatase and allows for a reconciliation of the contradictory published data. We suggest that varying surface energy contributions to the total energy of each phase as a function of size, rather than differing phase transition kinetics, is responsible for the enhanced pressure stability of anatase and specific structure selectivity of postanatase transitions.

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- ¹P. V. Kamat and N. M. Dimitrijevic, Sol. Energy 44, 83 (1990).
- ²A. L. Linsebigler, G. Q. Lu, and J. T. Yates, Chem. Rev. (Washington, D.C.) **95**, 735 (1995).
- ³R. J. Gonzalez and R. Zallen, in *Amorphous Insulators and Semi*conductors, edited by M. F. Thorpe and M. I. Mitkova (Kluwer Academic, Netherlands, 1997), pp. 395–403.
- ⁴M. Grätzel, Nature (London) **414**, 338 (2001).
- ⁵A. A. Gribb and J. F. Banfield, Am. Mineral. **82**, 717 (1997).
- ⁶H. Zhang and J. F. Banfield, J. Mater. Chem. **8**, 2073 (1998).
- ⁷K. Jacobs and A. P. Alivisatos, Rev. Mineral. Geochem. 44, 59 (2001).
- ⁸F. H. Pollak, in *Analytical Raman Spectroscopy*, edited by J. G. Grasselli and B. J. Bulkin (Wiley, New York, 1991).
- ⁹A. S. Pereira, C. A. Perottoni, and J. A. H. da Jornada, J. Raman Spectrosc. **34**, 578 (2003).
- ¹⁰H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39**, 625 (1981).
- ¹¹R. J. Nemanich, S. A. Solin, and R. M. Martin, Phys. Rev. B 23, 6348 (1981).
- ¹²K. K. Tiong, P. M. Amirtharaj, F. H. Pollak, and D. E. Aspnes, Appl. Phys. Lett. **44**, 122 (1984).
- ¹³C. J. Doss and R. Zallen, Phys. Rev. B 48, 15 626 (1993).
- ¹⁴W. S. O. Rodden, C. M. Sotomayor Torres, and C. N. Ironside, Semicond. Sci. Technol. **10**, 807 (1995).
- ¹⁵S. Kelly, F. H. Pollak, and M. Tomkiewicz, J. Phys. Chem. B 101, 2730 (1997).
- ¹⁶D. Bersani, P. P. Lottici, and X.-Z. Ding, Appl. Phys. Lett. **72**, 73 (1998).
- ¹⁷W. F. Zhang, Y. L. He, M. S. Zhang, Z. Yin, and Q. Chen, J. Phys. D **33**, 912 (2000).
- ¹⁸Z. Wang and S. K. Saxena, Solid State Commun. **118**, 75 (2001)
- ¹⁹G. R. Hearne, J. Zhao, A. M. Dawe, V. Pischedda, M. Maaza, M. K. Niewoudt, P. Kibasomba, O. Nemraoui, J. D. Comins, and M. J. Witcomb, Phys. Rev. B **70**, 134102 (2004).
- ²⁰Y. Lei, L. D. Zhang, and J. C. Fan, Chem. Phys. Lett. **338**, 231 (2001).
- ²¹E. Barborini, I. N. Kholmanov, P. Piseri, C. Ducati, C. E. Bottani,

- and P. Milani, Appl. Phys. Lett. 81, 3052 (2002).
- ²²J. C. Parker and R. W. Siegel, J. Mater. Res. **5**, 1246 (1990).
- ²³J. C. Parker and R. W. Siegel, Appl. Phys. Lett. 57, 943 (1990).
- ²⁴M. H. Lee and B. C. Choi, J. Am. Chem. Soc. **74**, 2309 (1991).
- ²⁵Y. S. Bobovich and M. Y. Tsenter, Opt. Spectrosc. **53**, 332 (1982).
- ²⁶W. Ma, Z. Lu, and M. Zhang, Appl. Phys. A: Mater. Sci. Process. 66, 621 (1998).
- ²⁷J. Muscat, V. Swamy, and N. M. Harrison, Phys. Rev. B 65, 224112 (2002).
- ²⁸N. A. Dubrovinskaia, L. S. Dubrovinsky, R. Ahuja, V. B. Prokopenko, V. Dmitriev, H.-P. Weber, J. M. Osorio-Guillen, and B. Johansson, Phys. Rev. Lett. **87**, 275501-1 (2001).
- ²⁹L. S. Dubrovinsky, N. A. Dubrovinskaia, V. Swamy, J. Muscat, N. M. Harrison, R. Ahuja, B. Holm, and B. Johansson, Nature (London) **410**, 653 (2001).
- ³⁰N. A. Bendeliny, S. V. Popova, and L. F. Vereschagin, Geokhimiya **1966**, 499 (1966).
- ³¹F. Dachille, P. Y. Simons, and R. Roy, Am. Mineral. **53**, 1929 (1968).
- ³²J. Haines and J. M. Léger, Physica B **192**, 233 (1993).
- ³³K. Lagarec and S. Desgreniers, Solid State Commun. 94, 519 (1995).
- ³⁴T. Arlt, M. Bermejo, M. A. Blanco, L. Gerward, J. Z. Jiang, J. Staun Olsen, and J. M. Recio, Phys. Rev. B **61**, 14414 (2000).
- ³⁵ H. Sato, S. Endo, M. Sugiyama, T. Kikegawa, O. Shimomura, and K. Kusaba, Science **251**, 786 (1991).
- ³⁶J. Tang and S. Endo, J. Am. Chem. Soc. **76**, 796 (1993).
- ³⁷J. S. Olsen, L. Gerward, and J. Z. Jiang, J. Phys. Chem. Solids 60, 229 (1999).
- ³⁸S. C. Liao, Y. J. Chen, W. E. Mayo, and B. H. Kear, Nanostruct. Mater. **11**, 553 (1999).
- ³⁹Z. Wang, S. K. Saxena, V. Pischedda, H. P. Liermann, and C. S. Zha, J. Phys.: Condens. Matter **13**, 8317 (2001).
- ⁴⁰ V. Swamy, L. S. Dubrovinsky, N. A. Dubrovinskaia, A. S. Simionovici, M. Drakopoulos, V. Dmitriev, and H. P. Weber, Solid State Commun. **125**, 111 (2003).

- ⁴¹T. Sekiya, M. Okumura, S. Kurita, and N. Hamaya, High Press. Res. **23**, 333 (2003).
- ⁴²A. C. Withers, E. J. Essene, and Y. Zhang, Contrib. Mineral. Petrol. **145**, 199 (2003).
- ⁴³T. Sekiya, S. Ohta, S. Kamei, M. Hanakawa, and S. Kurita, J. Phys. Chem. Solids **62**, 717 (2001).
- ⁴⁴D. M. Shchukin, J. H. Schattka, M. Antonietti, and R. A. Caruso, J. Phys. Chem. B **107**, 952 (2003).
- ⁴⁵ http://www.milleniumchem.com
- ⁴⁶R. A. Caruso, M. Antonietti, M. Giersig, H.-P. Hentze, and J. Jia, Chem. Mater. **13**, 1114 (2001).
- ⁴⁷ http://www.altairnano.com
- ⁴⁸D. Machon, V. V. Sinitsyn, V. P. Dmitriev, I. K. Bdikin, L. S. Dubrovinsky, I. V. Kuleshov, E. G. Ponyatovsky, and H. P. Weber, J. Phys.: Condens. Matter **15**, 7227 (2003).
- ⁴⁹A. Savitsky and M. J. E. Golay, Anal. Chem. **36**, 1627 (1964).
- ⁵⁰N. A. Dubrovinskaia and L. S. Dubrovinsky, Rev. Sci. Instrum. 74, 3433 (2003).
- ⁵¹H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res., [Oceans] **91**, 4673 (1986).

- ⁵²I. R. Beattie and T. R. Gilson, Proc. R. Soc. London, Ser. A **307**, 407 (1968).
- ⁵³T. Ohsaka, F. Izumi, and Y. Fujiki, J. Raman Spectrosc. 7, 321 (1978).
- ⁵⁴ M. Mikami, S. Nakamura, O. Kitao, and H. Arakawa, Phys. Rev. B 66, 155213 (2002).
- ⁵⁵H. Berger, H. Tang, and F. Lévy, J. Cryst. Growth **130**, 108 (1993).
- ⁵⁶T. Ohsaka, S. Yamaoka, and O. Shimomura, Solid State Commun. **30**, 345 (1979).
- ⁵⁷ V. Swamy and L. S. Dubrovinsky, J. Phys. Chem. Solids **62**, 673 (2001).
- ⁵⁸P. Gillet, R. J. Hemley, and P. F. McMillan, Rev. Mineral. **37**, 525 (1998).
- ⁵⁹X. M. Wu, Y. Y. Di, Z. C. Tan, and S. S. Qu, J. Inorg. Mater. (Chinese), **16**, 159 (2001).
- ⁶⁰G. Grimvall, *Thermophysical Properties of Materials* (North-Holland, New York, 1986).
- ⁶¹L. G. Liu and T. P. Mernagh, Eur. J. Mineral. 4, 45 (1992).