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# Compressibility of Nanocrystalline $TiO_2$ Anatase

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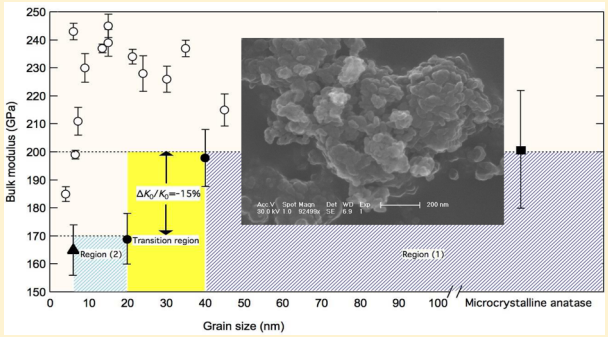
**ABSTRACT:** Using high-resolution, synchrotron-based powder X-ray diffraction (XRD), we have studied the high-pressure behavior of the anatase phase of nanocrystalline $TiO_2$ (nc-$TiO_2$) under hydrostatic conditions. We find that for anatase with a grain size larger than ~40 nm, the room-pressure bulk modulus $K_0$ remains constant at ~200 GPa to within experimental uncertainties. An ~15% decrease in $K_0$ is observed for grains that are ~20 nm in size and remains unchanged for grains down to 6 nm in diameter, indicating a rapid increase in compressibility for nc-$TiO_2$ anatase between 40 and 20 nm.




## INTRODUCTION

$TiO_2$ anatase is an important material in many technological applications including photocatalysis, ceramics, electronic storage media, and hydrogen storage applications.[1−3] Due to its promising technological applications,[1−3] the high-pressure behavior of nc-$TiO_2$ anatase has attracted great interest over the past decade[4−17] with studies focusing on pressure-induced phase transitions and amorphization.[5−7,9,11,12,14−17] However, little is known about the effect of particle size on the equation of state (EOS) of $TiO_2$ anatase and the few available studies are inconclusive and controversial: previous experiments on nc-$TiO_2$ anatase have found that the bulk modulus may increase or decrease with decreasing particle size.[4,8,10,13] Some of the complications likely arise from the lack of hydrostaticity in the sample under pressure,[8,10] whereas other studies do not provide the EOS of nc-$TiO_2$ anatase[13] or have some important issues (e.g., typographical errors or mistakes in EOS determination) in the reported EOS and/or measured value of its zero-pressure volume $V_0$.[4] Thus, a consistent understanding of the behavior of nanocrystalline $TiO_2$ anatase as grain size is changed is presently lacking.

To eliminate, or at least reduce, the controversy regarding the grain size dependence, we study the size dependence of the bulk modulus in nc-$TiO_2$ anatase under hydrostatic conditions at pressures up to ~11 GPa. Therefore, this work along with a reanalysis of previous studies on nc-$TiO_2$ anatase[4,8,10,13] allow us to reach consistency among several studies of the size dependence of the bulk modulus of nc-$TiO_2$ anatase.

## EXPERIMENTAL METHODS

Nanocrystalline samples of 99% $TiO_2$ anatase/rutile powder (Nanostructured & Amorphous Materials, Inc., 50 nm average particle size) and 99.7% $TiO_2$ anatase powder (Alfa Aesar, 15 nm average particle size) were used as starting materials in our diamond-anvil cell (DAC) experiments. We confirmed the grain sizes by using the full-width-half-maximum[18] of the XRD peaks to be 40(±3) and 20(±4) nm, respectively, consistent with scanning electron microscope measurements which yielded particle sizes of ~40−60 and ~20−30 nm, respectively. We performed two independent room temperature, high-pressure DAC experiments to study the EOS of nc-$TiO_2$ anatase (Table 1). A mixture of methanol−ethanol−water (M-E-W) (16:3:1 by volume) was used as the pressure medium.[19] For pressures up to ~11 GPa, M-E-W is hydrostatic.[20,21] Rhenium and stainless steel gaskets of initial thicknesses of 270 $\mu$m were precompressed to thicknesses of 30 $\mu$m. The sample, pressure calibrant ruby,[22] and pressure medium were placed in a 120 or 150 $\mu$m sample chamber in the center of the gasket and compressed between a pair of matched 300 $\mu$m culet diamonds. We collected angular-dispersive XRD at room temperature (Figure 1) using a MAR CCD at the HPCAT-IDB beamline ($\lambda$ = 0.39779 Å) at the Advanced Photon Source (APS) at Argonne National Laboratory, and a MAR345 imaging plate at the B2 beamline ($\lambda$ = 0.49594 Å), Cornell High Energy Synchrotron Source (CHESS), Cornell University. The pressure−volume ($P$−$V$) data nc-$TiO_2$ anatase phase was fit by using a second-order Birch−Murnaghan EOS (BM-EOS),[23] where the first pressure derivative of the bulk modulus $K_0'$ is fixed to 4 to more easily compare with previous studies (Table 1). Other details on the experimental methods can be found elsewhere.[24−26]

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Table 1. The EOSs for nc-$TiO_2$ Anatase and the Associated Experimental Conditions[a]

| grain size (nm) | $V_0$ (Å$^3$) | $K_0$ (GPa) | $K_0'$ | pressure range (GPa) | pressure medium | ref | notes |
|---|---|---|---|---|---|---|---|
| 40 | 34.06(0.04) | 198(10) | 4 | 0−11 | M-E-W (16:3:1) | this study | |
| 20 | 34.14(0.05) | 169(9) | 4 | 0−11 | M-E-W (16:3:1) | this study | |
| 30−40 | 34.04 | 243(3) | 4 | 0−16 | no medium | ref 10 | Nonhydrostatic compression |
| 6 | NA | 237(3) | 4 | 0−18 | fluorinert FC70-FC77 (1:1) | ref 8 | Nonhydrostatic compression above~2.5 GPa |
| 6 | 34.18 | 176(15) | 4 | 0−23 | M-E-W (16:3:1) | ref 13 | - The EOS is not given in this ref |
| | | 165(9) | 4 | 0−9 | | | - We compute the EOS from the given $P-V$ data |
| | | 165(8) | 4 | 0−13 | | | - $V_0$ is determined from the 5 $d$-spacings given in this ref |
| | | 168(10) | 4 | 0−17 | | | |
| | | 171(12) | 4 | 0−19 | | | |
| 6.5 | NA | 199(1.5) | NA | 0−12 | M-E (4:1) | ref 4 | - $V_0$ for the 15 nm grain size is too low and contradicts findings |
| 15 | 33.81 | 239(4.8) | NA | 0−12 | | | |
| | | 245(4.2) | NA | 5−12 | | | - $K_0'$ is not given in this ref |
| | | 222(12)* | 4* | | | | - The 5−12 GPa for the 15 nm grain size is where our $P-V$ data agree with this ref and we have used our $V_0$ for the 20 nm size to fit a second-order BM-EOS |
| | | 200(10)* | 12.27* | | | | |
| | 34.14* | 173(13)* | 4* | | | | |
| 4 | NA | 185(2.6) | NA | NA | | | |
| 7.2 | NA | 211(5) | NA | NA | | | |
| 9 | NA | 230(5.1) | NA | NA | | | |
| 13.5 | NA | 237(1.5) | NA | NA | | | |
| 21.3 | NA | 234(2.6) | NA | NA | | | |
| 24 | NA | 228(6.3) | NA | NA | | | |
| 30.1 | NA | 226(4.6) | NA | NA | | | |
| 45 | NA | 215(5.7) | NA | NA | | | |
| micro-crystalline | 34.07 | 190(10) | 5.3 (0.1) | 0−14 | M-E-W (16:3:1) | ref 27 | |
| | | 201(21)* | 4* | | | | |

[a]The EOSs were obtained from a second-order BM-EOS[23] (with $K_0' = 4$). For comparison, we list other experimental results.[4,8,10,13,27] Where the $K_0'$ value is given as 4; this value is fixed for the calculation. 1$\sigma$ uncertainties are given in parentheses. For values not given, NA is shown. An asterisk indicates a revised EOS, using a second-order BM-EOS.[23]

## RESULTS AND DISCUSSION

In all experimental runs, nc-$TiO_2$ anatase was stable up to the maximum pressure in this study of ~11 GPa (Figures 1−3). The sample with 20 nm average particle size shows an ~15% reduction in bulk modulus as compared to the sample with an average particle size of 40 nm (Table 1, Figure 2). Our measured second-order BM-EOS[23] for the 40 nm nc-$TiO_2$ anatase gives a bulk modulus $K_0$ = 198(10) GPa with $V_0$ = 34.06(0.04) Å$^3$/f.u.; whereas for the 20 nm size, we obtain a significantly lower value of $K_0$ = 169(9) GPa with $V_0$ = 34.14(0.05) Å$^3$/f.u. (Table 1, Figure 2).

In our study, the bulk moduli of nc-$TiO_2$ anatase for both sizes are significantly smaller than those reported previously.[8,10] The reported $K_0$ values in these studies are 237(3) and 243(3) GPa when $K_0'$ is fixed to 4 for 6 nm[8] and 30−40 nm[10] grains, respectively (Table 1). Thus, despite the significant grain size difference in these studies,[8,10] the bulk modulus appears to be almost size independent and much higher than that of the microcrystalline value of ~200 GPa[27] (Table 1). However, both studies[8,10] suffered from nonhydrostatic compression conditions (Figure 2). No pressure medium was used in ref 10, whereas in ref 8, a Fluorinert FC70-FC77 (1:1) mixture was used. In the latter study, the hydrostaticity limit of the pressure medium does not exceed 2.5 GPa,[28,29] which is clearly visible as a kink in the corresponding $P-V$ diagram at ~2 GPa (Figure 2a). The nonhydrostatic conditions have an effect on the EOS because of the systematic error introduced in the determined pressure of the material.[30−32] Additionally, in a comparison with available data on the compressional behavior of nc-$TiO_2$ anatase for sizes as low as 6 nm[4,13] (Figure 2a) and for other nc-$TiO_2$ phases,[33,34] no such kink is observed. Consequently, nonhydrostaticity is likely responsible for the significant overestimation of the bulk modulus.[8,10]

A recent study[4] explored the effect of grain size on nc-$TiO_2$ anatase on the bulk modulus under hydrostatic conditions and reported a critical size of 15 nm below which $K_0$ decreases (Table 1, Figure 2b). However, the measured bulk moduli in this study[4] require further analyses as $K_0$ obtained from a BM-EOS is very sensitive to both $V_0$ and $K_0'$.[23] The reported value of $V_0$ (Table 1, Figure 2a) is inconsistent with previous measurements of nc-$TiO_2$ anatase,[13,35,36] where $V_0$ increases as grain size decreases; ref 4 finds the opposite behavior. Moreover, $K_0'$ is not reported,[4] thus a true comparison cannot be made on the size dependence of the bulk modulus (Table 1). However, the $P-V$ data of the 15 nm grains (ref 4) agree with our 20 nm size at $P$ > 4 GPa (Figure 2a). Therefore, if we


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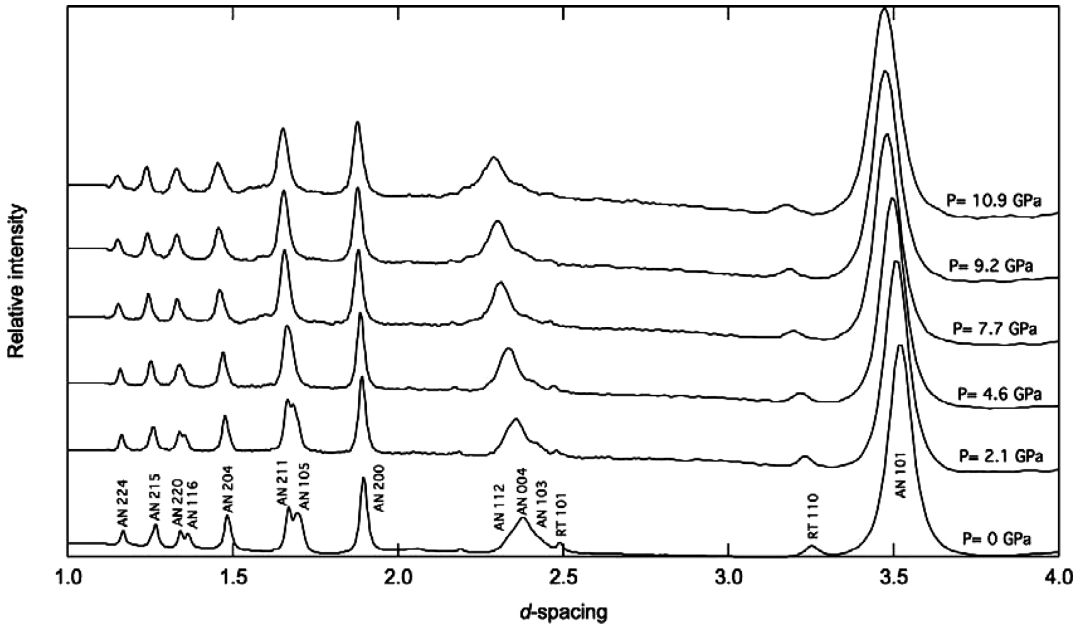


**Figure 1.** XRD patterns at various pressures during compression of nc-$TiO_2$ anatase of 20 nm grain size up to 10.9 GPa show the corresponding *hkl* values for anatase (AN) and rutile (RT).

use our $V_0$ = 34.14 Å$^3$ for the 20 nm size and fit a second-order BM-EOS[23] for the high-pressure data of ref 4 (i.e., for $P$ > 4 GPa), we obtain $K_0$ = 173(13) GPa, in excellent agreement with our measured value (Table 1) and ∼28% lower than the reported values in ref 4 of $K_0$ = 239−245 GPa for the 15 nm grain size. Hence, an increase of $V_0$ by 1%, for consistency with our study and others,[13,35,36] leads to a significant reduction of the bulk modulus. On the other hand, if we fit a second-order BM-EOS to the entire pressure range, we obtain a $K_0$ = 222 GPa (Table 1), still an ∼8% reduction in comparison to the reported values. The reported $K_0$ values are 215(5.7) and 234(2.6) GPa for 45 and 21.3 nm average particle size, respectively.[4] For similar sizes, our bulk moduli are 198(10) and 169(9) GPa (Table 1). Notably, the $K_0$ value for the 6.5 nm is ∼20% higher than the value we compute for the 6 nm size[13] (Table 1). However, while the data given in ref 4 are insufficient for a detailed reanalysis of the EOSs for each particle size, we suspect that a significant reduction of $K_0$, similar to that for the 15 nm particle size, may also occur. Thus, in comparison to ours and another recent study[13] where hydrostatic conditions are present, $K_0'$ is constrained and $V_0$ is consistent with previous studies,[35,36] ref 4 may significantly overestimate $K_0$ for nc-$TiO_2$ anatase, which is at least partly due to the choice of $K_0'$ as well as $V_0$ as discussed above.

In a recent study on the hydrostatic compressional behavior of 6 nm $TiO_2$ anatase,[13] we find excellent agreement with our results for the 20 nm grain size (Figure 3, Table 1). In addition to the similar hydrostatic conditions, the larger $V_0$ value reported in this study is consistent with ours and previous measurements of nc-$TiO_2$ anatase[35,36] (Table 1). The change in normalized lattice parameters ($a/a_0$ and $c/c_0$) with pressure in ref 13 is also in good agreement with ours (Figure 3b), where $c$ is much more compressible than $a$. However, the focus of ref 13 was on the unusual compressional behavior of nc-$TiO_2$ anatase but without an EOS determination. We, thus, have computed the EOS for the 6 nm anatase from ref 13 (Table 1) and find excellent agreement with our measured $K_0$ for the 20 nm size; the computed value of $K_0$ has a value of ∼170 GPa with $K_0'$ fixed to 4 regardless of the choice of the pressure range used to fit the second-order BM-EOS[23] (Table 1). In detail, $K_0$ = 165(9) GPa for $P$-range up to ∼9 GPa, where the M-E-W pressure medium is still hydrostatic, and $K_0$ = 176(15) GPa for the whole $P$-range up to ∼23 GPa (Table 1). Thus, despite the small kink observed at pressures of 10−12 GPa,[13] likely due to freezing of M-E-W pressure medium,[20,21] the bulk moduli are consistent with our value of 169(9) GPa (Table 1). Thus, we conclude that the bulk modulus of anatase does not change for grain sizes between 6 and 20 nm. It has been suggested that at this small grain size, nc-$TiO_2$ anatase is too small to sustain high dislocation concentrations, which is consistent with the observed reduction of the bulk modulus.[4] The surface of the nc-$TiO_2$ particles consists most likely of undersaturated oxygen and/or titanium sites. Therefore, these sites may undergo reactions with the M-E-W pressure medium. However, we do not observe $OH^-$ contamination through asymmetry in the XRD peaks and this effect is likely not dominant. An alternative mechanism is that the thickness of the strained surface layer is sufficiently large that it can affect the bulk modulus directly.[37] With decreasing particle size we observe an increased effective volume relative to the microcrystalline reference (Table 1) suggesting the presence of an extensive (average) strain. We attribute the unexpectedly large reduction in bulk modulus to a significantly strained outer shell of the particles. Assuming that the thickness of the strained shell depends weakly on the size of the particle, it follows as the volume fraction of the shell relative to the particle volume increases with decreasing particle size that the bulk modulus reduction should become more pronounced. However, if this trend continues for very small particle size, where the energetics of the strained shell may promote restructuring, remains unclear.

The measured bulk modulus of microcrystalline bulk $TiO_2$ anatase of ∼200 GPa[27] (Table 1) is in good agreement with our $K_0$ for the 40 nm grain size. Both, ours (40 nm) and previous bulk anatase,[27] show similar compressional behavior (Figure 2b). Since the 40 nm anatase behaves like microcrystalline samples, we conclude that the bulk modulus of anatase is size-


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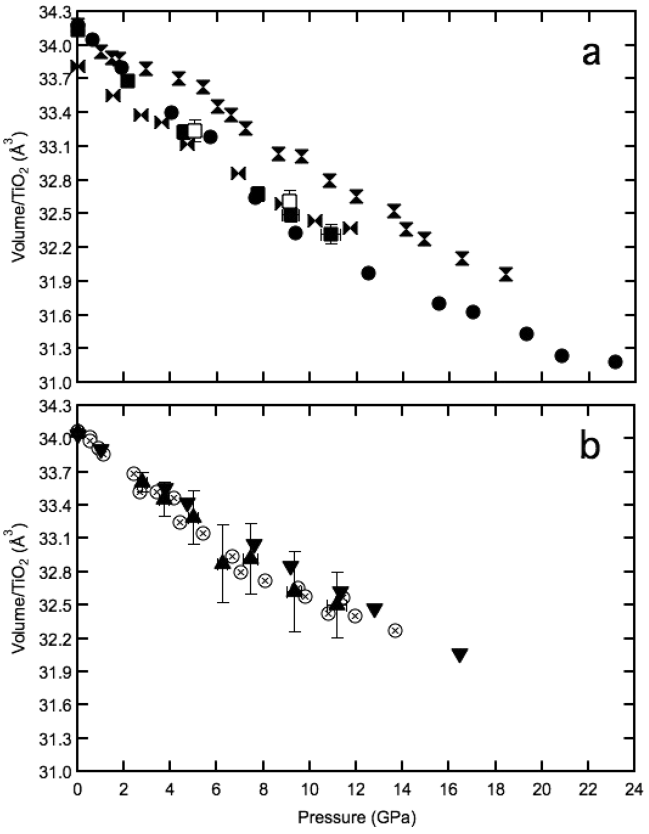


**Figure 2.** Pressure versus volume of one $TiO_2$ unit for nanocrystalline anatase for 20 (squares) and 40 nm (triangles) sizes. The solid symbols indicate points under compression, and open symbols indicate points upon decompression. (a) For the 20 nm grain size, our high-pressure volumes are smaller than previous work shown[8] (vertical bowties). $V_0$ in ref 8 is not given, thus we assumed the same value as measured by ref 13 for the same grain size. $V_0$ of 15 nm grain size[4] (horizontal bowties) is smaller than our $V_0$ and is inconsistent with $V_0$ measurements of nc-$TiO_2$ anatase.[13,35,36] (b) Our high-pressure volumes are smaller than previous work[10] on 30−40 nm (inverted triangles). The compression behavior of our 40 nm grain size is similar to that of microcrystalline $TiO_2$ (crossed circles[27]).

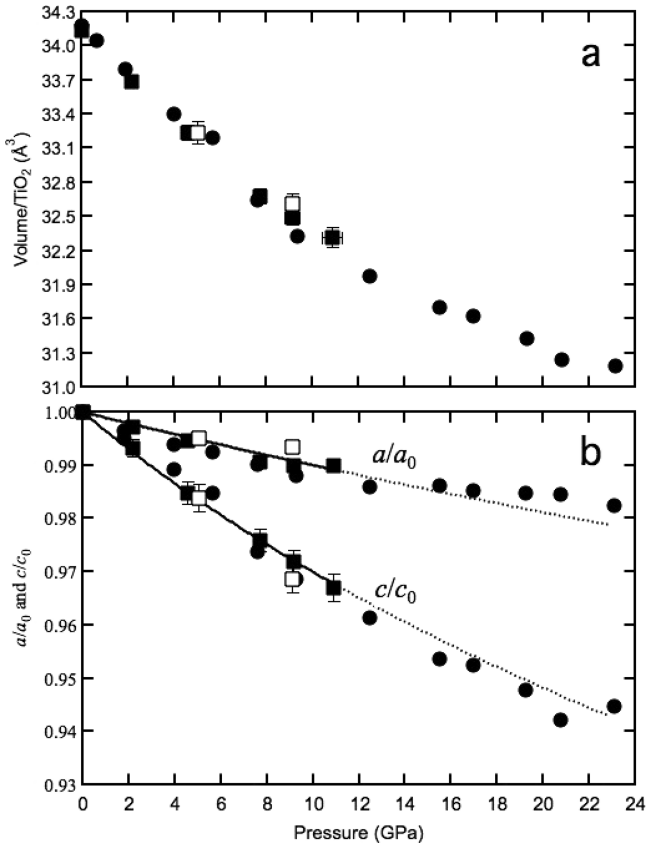


**Figure 3.** (a) The compression behavior of our 20 nm grain size is in good agreement with the 6 nm size previously observed[13] (circles). (b) The change in the normalized unit cell parameters ($a/a_0$ and $c/c_0$) as a function of pressure. Refer to Figure 2 caption for symbol identification. Solid lines indicate the linear BM-EOS[53] for $a$ and $c$ axes up to ∼11 GPa. The dashed curve is extrapolated from the linear BM-EOS fit[53] and shows good agreement beyond the hydrostatic limit of M-E-W as well as with a previous study.[13].

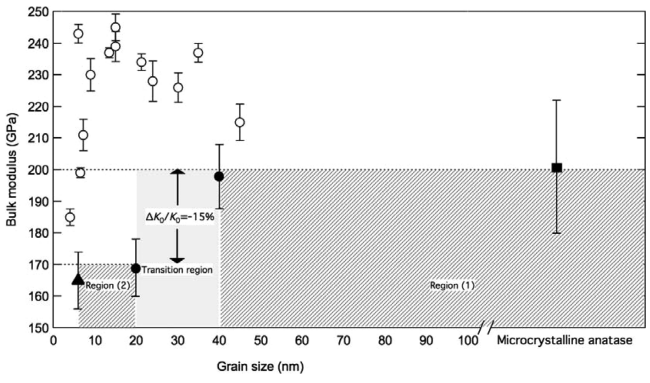


**Figure 4.** The change in bulk modulus of anatase as a function of grain size. Closed symbols show our values (circles) and those of the microcrystalline $TiO_2$ anatase (square[27]) and of 6 nm nc-$TiO_2$ anatase (triangle[13]). The bulk modulus of anatase is size-independent in, at least, two regions: from microcrystalline size down to 40 nm and from 6 to 20 nm. The region between 20 and 40 nm indicates a transition region for nc-$TiO_2$ anatase. To compare, we show previously reported values (open circles[4,8,10]).

independent for grain sizes larger than ∼40 nm (Figure 4). On the other hand, for smaller grain sizes we find a much lower $K_0$ as compared to the 40 nm sample, suggesting that in the size range of 20−40 nm, the compressibility of nc-$TiO_2$ anatase rapidly changes by ∼15% (Figure 4).

The observed decrease in $K_0$ of $TiO_2$ anatase as the particle size is reduced is consistent with previous observations for some other oxides and metals (e.g., $ZrO_2$,[38,39] $SnO_2$,[40] $Al_2O_3$,[41] MgO,[42] ZnO,[43] and Ni[44]), although this is not a universal behavior (e.g., CuO[45] and Fe[46] are size-independent, whereas $K_0$ increases as particle size is reduced in $Fe_2O_3$,[47] Ag,[48] and Au[48]). We should also note that although the bulk modulus of anatase decreases with grain sizes <40 nm, this is not necessarily evidence for an inverse Hall−Petch effect,[49,50] as the bulk modulus is not a good indicator for hardness, instead the shear modulus is a better measure of hardness.[24,26,51,52] Thus, measurements on the grain size dependence of the shear modulus of nc-$TiO_2$ anatase are necessary to examine whether anatase follows an inverse Hall−Petch effect or not.

## CONCLUSIONS

In summary, using powder XRD, we have studied the compressional behavior and the size dependence on the bulk


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modulus of nc-$TiO_2$ anatase. While the grain size dependence of the bulk modulus has been controversial, we provide a consistent understanding for the size dependence of the bulk modulus of anatase: (1) for grain sizes >∼40 nm (2) and grain sizes from 6 to 20 nm, the bulk modulus is size independent. Between region (1) and region (2), the bulk modulus decreases by ∼15%, indicating a strong dependence of bulk modulus on particle size in the size range between 20 and 40 nm.

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### Notes

The authors declare no competing financial interest.

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