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Anisotropy of elastic properties of disordered cubic titanium monoxide TiO_y

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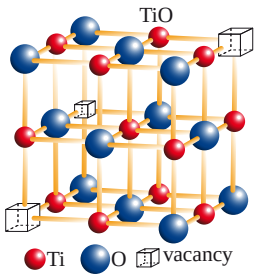
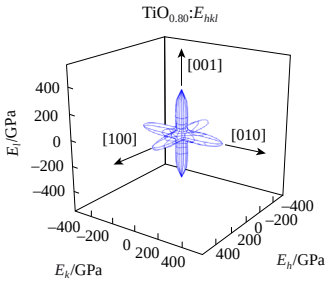
For the first time, the elastic constants c_{11}, c_{12} and c_{44} of disordered cubic titanium monoxide TiO_y were determined depending on the oxygen content y in the homogeneity region from $TiO_{0.80}$ to $TiO_{1.25}$. It has been established that the values of the elastic moduli depend on the oxygen content y and the crystallographic direction [hkl]. Large changes in the elastic characteristics of TiO_y depending on the [hkl] direction indicate a strong anisotropy of the elasticity of disordered cubic titanium monoxide.





Keywords: titanium monoxide, hardness, elastic constants, elastic moduli, nonstoichiometry, anisotropy of elastic properties, ductile material.

Nonstoichiometric cubic titanium monoxide TiO_y with a $B1$ type structure belongs to strongly nonstoichiometric interstitial compounds, has a wide homogeneity region from $TiO_{0.80}$ to $TiO_{1.25}$ and contains a large number of structural vacancies in both nonmetallic and metallic sublattices.[1] Vacant octahedral interstices in the oxygen sublattice of disordered cubic titanium monoxide TiO_y can be filled with other nonmetallic interstitial atoms, for example, hydrogen H.[2] Interestingly, nanoparticles of amorphous titanium dioxide TiO_2 also contain vacancies in the titanium and oxygen sublattices.[3] All properties of nonstoichiometric cubic titanium monoxide TiO_y depend on the relative oxygen content y and change markedly in the region of its homogeneity.

Information about the mechanical properties of disordered titanium monoxide is limited to measurements of the microhardness of quenched TiO_y samples in the range $0.92 \leqslant y \leqslant 1.26$: with increasing y, a nonlinear increase in microhardness is observed.[4] The technical application of disordered titanium monoxide is related to its mechanical properties. However, there are no experimental data on the dependence of the elastic properties of disordered titanium monoxide TiO_y on the oxygen content y.

Theoretical calculations of elastic characteristics are known only for equiatomic quasi-stoichiometric titanium monoxide $TiO_{1.00}$. Theoretical estimates of elastic properties are obtained in different versions of the density functional theory using the local density and generalized gradient approximations. The elastic stiffness constants c_{ij} of the equiatomic quasi-stoichiometric titanium monoxide $TiO_{1.00}$ are reported,[5–9] which indicate a very noticeable anisotropy of the elasticity of cubic titanium monoxide TiO.

The elastic matrix of cubic crystals includes three independent elastic constants c_{11}, c_{12} and c_{44}. To take into account the anisotropy of elasticity of nonstoichiometric cubic titanium monoxide TiO_y, it is necessary to know how the elastic constants c_{11}, c_{12} and c_{44} change depending on the oxygen content y. In this regard, the main goals of this work are to quantify the elastic constants of nonstoichiometric titanium monoxide TiO_y using experimental results[2] on the microhardness of disordered TiO_y with different oxygen content, as well as to assess the elasticity anisotropy of nonstoichiometric disordered cubic titanium monoxide TiO_y.

Teter's study[10] of the hardness of carbides, nitrides and other compounds revealed a general tendency for their hardness H_V to decrease with a decrease in the shear modulus G and bulk modulus B. Other work[11] showed that the correlation between hardness H_V and shear modulus G of these compounds, established by Teter,[10] can be represented in the form of a linear relationship $H_V = 0.151G$. In the case of nonstoichiometric compounds, the use of this relationship makes it possible to find the change in the shear modulus $G(y)$ depending on the composition of disordered TiO_y based[4] on the change in its microhardness as

$$G(y) = H_V(y)/0.151. \quad (1)$$

Numerical approximation of the values of the shear modulus $G(y)$, calculated from equation (1) using experimental values[4] of the microhardness of disordered TiO_y with different oxygen content, allowed us to obtain the following empirical dependence

$$G(y) = -250.7 + 555.1y - 227.0y^2 = G_{y=1}(-3.23902 + 7.17183y - 2.93282y^2), \quad (2)$$

where $G_{y=1} = 77.4$ GPa is the shear modulus of stoichiometric titanium monoxide $TiO_{1.00}$.

In the mentioned work,[11] an empirical function $H_V = 2(k^2G)^{0.585} - 3$ was proposed, relating the microhardness H_V to the shear modulus G. The coefficient k is equal to the ratio of the shear and bulk moduli, *i.e.*, $k = G/B$. From this empirical function[11] it follows that

$$B(y) = [G(y)]^{3/2}/\{[H_V(y) + 3]/2\}^{1.17}. \quad (3)$$

Numerical approximation of the values of the bulk modulus $B(y)$, calculated according to equation (3) using experimental values[4]

of microhardness H_V of disordered TiO_y with different oxygen content, made it possible to obtain a quantitative empirical dependence $B(y)$ in the form

$$B(y) = -322.3 + 757.2y - 311.1y^2 = B_{y=1}(-2.60339 + 6.11632y - 2.51292y^2). \quad (4)$$

The found bulk modulus $B_{y=1}$ of stoichiometric $TiO_{1.00}$ is 123.8 GPa. The errors in determining $G(y)$ and $B(y)$ are ±10.0 GPa.

To move from the found quantitative dependences of the moduli $G(y)$ and $B(y)$ of titanium monoxide to its elastic stiffness constants c_{11}, c_{12} and c_{44}, we further applied the approach proposed and developed earlier in our work[12] on the nonstoichiometry and elasticity of disordered cubic titanium carbide TiC_y.

The bulk modulus of isotropic cubic single crystals can be expressed as $B = (c_{11} + 2c_{12})/3$. To a first approximation, the dependence of $B(y)$ of single-crystal particles of titanium monoxide TiO_y on the oxygen content y has the same form as the dependence of $B(y)$ [equation (4)]. With this in mind, $(c_{11} + 2c_{12})/3 = B_{y=1}(-2.60339 + 6.11632y - 2.51292y^2)$. A comparison of the moduli B and G of quasi-stoichiometric $TiO_{1.00}$ theoretically calculated in the above works[3–7] with the found values of $G_{y=1}$ = 77.4 GPa and $B_{y=1}$ = 123.8 GPa shows that the theoretical values of the moduli $G_{calc,\ y=1}$ = 78 GPa and $B_{calc,\ y=1}$ = 205 GPa of quasi-stoichiometric $TiO_{1.00}$, calculated earlier,[9] are closest to our estimates of $G_{y=1}$ and $B_{y=1}$. Taking into account the numerical values[7] of the elastic moduli $B_{calc,y=1}$ = 205 GPa and $G_{calc,y=1}$ = 78 GPa and the elastic constants c_{11} = 511 GPa, c_{12} = 53 GPa and c_{44} = 31 GPa of equiatomic stoichiometric titanium monoxide, it is possible to establish empirical relationships between the theoretical elastic constants $c_{ij,\ y=1}$ and the theoretical bulk and shear moduli of stoichiometric $TiO_{1.00}$ presented in a recent paper.[9] These ratios are $c_{11,y=1} = 2.49268B_{calc,\ y=1}$, $c_{12,\ y=1} = 0.25854B_{calc,y=1}$ and $c_{44,\ y=1} = 0.39744G_{calc,\ y=1}$. The dependences of the elastic constants c_{11} and c_{12} on the composition of nonstoichiometric compounds are qualitatively the same.[12] From which it follows that the elastic constants $c_{11}(y)$ and $c_{12}(y)$ as functions of the composition of disordered titanium monoxide TiO_y have the form

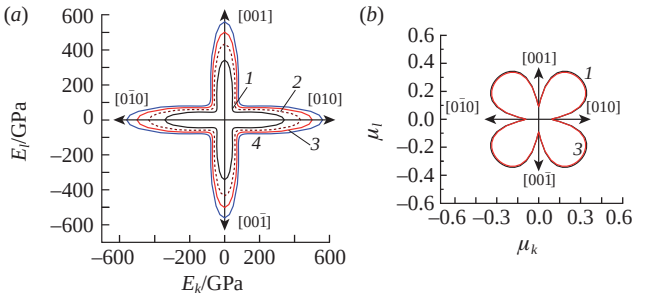


Figure 1 Dependences of (*a*) Young's modulus *E* and (*b*) Poisson's ratio μ of cubic titanium monoxide TiO_y with (*1*) y = 0.8, (*2*) y = 0.9, (*3*) y = 1.0 and (*4*) y = 1.2 on the direction [*hkl*] in the plane (100).

$$c_{11}(y) = c_{11,\ y=1}(-2.60339 + 6.11632y - 2.51292y^2), \quad (5)$$

$$c_{12}(y) = c_{12,\ y=1}(-2.60339 + 6.11632y - 2.51292y^2), \quad (6)$$

where $c_{11,y=1}$ = 511 GPa and $c_{12,\ y=1}$ = 53 GPa. The errors in determining $c_{11}(y)$ and $c_{12}(y)$ are ±10.0 GPa.

According to the cited work,[5] the resistance of a cubic crystal to shear distortion is characterized by the shear constant c_{44}. The found change $G(y)$ [equation (2)] represents the averaged concentration dependence of the shear modulus, since it was obtained from the microhardness dependence[2] $H_V(y)$ of TiO_y measured on polycrystalline samples. Therefore, the dependence $G(y)$ of single-crystal TiO_y particles on the oxygen content y has the same form as the dependence $G(y)$ [equation (2)], and the elastic constant $c_{44}(y)$ of disordered TiO_y is described with an accuracy of ±10.0 GPa by a function of the form

$$c_{44}(y) = c_{44,\ y=1}(-3.23902 + 7.17183y - 2.93282y^2), \quad (7)$$

where $c_{44,\ y=1}$ = 31 GPa.

Previous work[13] presents the dependences of Young's modulus E_{hkl}, Poisson's ratio μ_{hkl} and shear modulus G_{hkl} of cubic crystals on

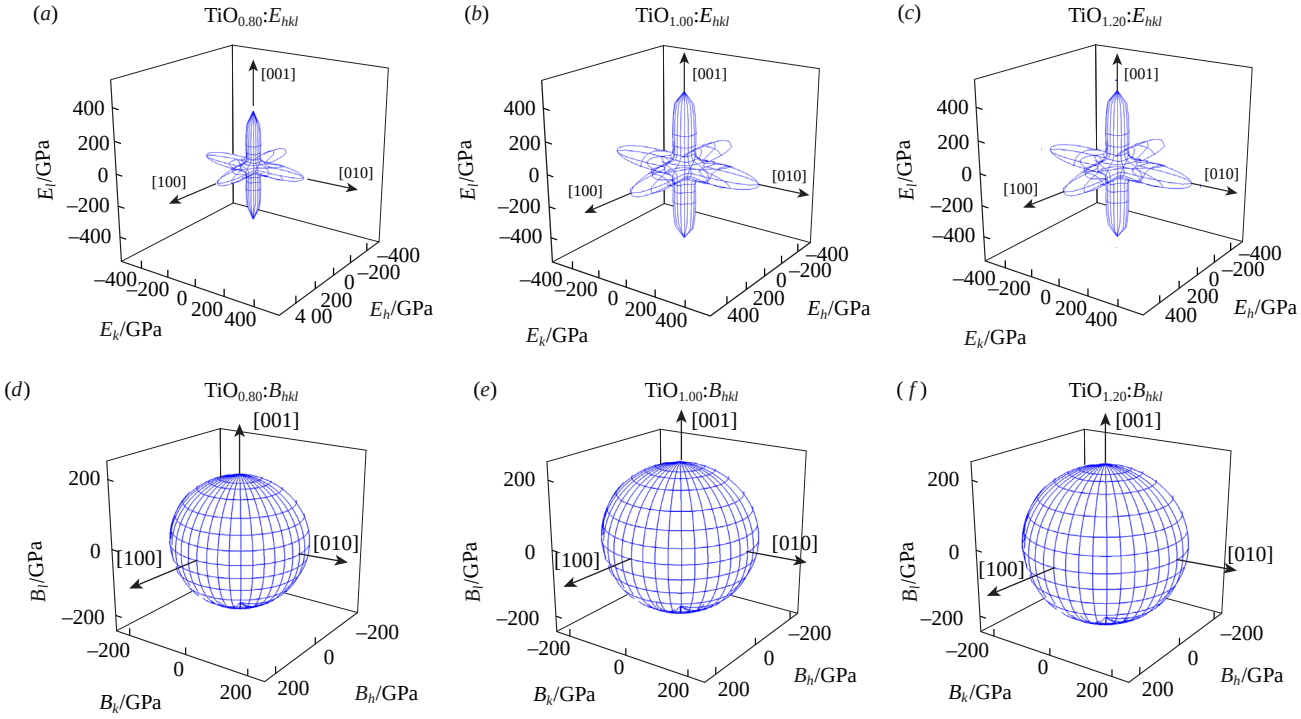


Figure 2 The spatial distributions of (*a*)–(*c*) Young's modulus E_{hkl} and (*d*)–(*f*) bulk modulus B_{hkl} of disordered cubic titanium monoxides (*a*),(*d*) $TiO_{0.80}$, (*b*),(*e*) $TiO_{1.00}$ and (*c*),(*f*) $TiO_{1.20}$ with different oxygen contents.

the crystallographic direction [*hkl*], which indicates their anisotropy. These elastic characteristics of cubic crystals, taking into account the anisotropy factor $\Gamma = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2$, are functions of the elastic constants c_{11}, c_{12} and c_{44}:[13]

$$E_{hkl} = \frac{(c_{11} - c_{12})(c_{11} + 2c_{12})c_{44}}{(c_{11} + c_{12})c_{44} - (2c_{44} - c_{11} + c_{12})(c_{11} + 2c_{12})\Gamma}. \quad (8)$$

To calculate the distributions of elastic characteristics of single-crystal cubic titanium monoxide TiO_y depending on the direction [*hkl*] and oxygen content *y* using equation (8) and analogous equations for Poisson's ratio μ_{hkl} and bulk modulus B_{hkl}, the found concentration dependences $c_{ij}(y)$ [equations (5)–(7)] of disordered cubic titanium monoxide TiO_y were used. Figure 1 shows the constructed distributions of Young's modulus $E_{hkl}(y)$ and Poisson's ratio $\mu_{hkl}(y)$ in the (100) plane of cubic titanium monoxide TiO_y with different oxygen content *y*. The distribution of Poisson's ratio $\mu_{hkl}(y)$ is shown only for *y* equal to 0.8 and 1.0.

The value of Young's modulus E_{hk0} in the (100) plane of $TiO_{0.80}$, corresponding to the lower boundary of the homogeneity region of the disordered cubic phase, varies from ~341 to ~70 GPa. For equiatomic titanium monoxide $TiO_{1.00}$, Young's modulus varies from ~499 to ~111 GPa, and for $TiO_{1.20}$, Young's modulus varies from ~558 to ~128 GPa [Figure 1(*a*)]. Poisson's ratio μ in the (100) plane of titanium monoxides, depending on the [*hkl*] direction, varies from ~0.094 to ~0.417 and is almost independent of the composition of TiO_y [Figure 1(*b*)]. The bulk modulus *B* of cubic titanium monoxide does not depend on the [*hkl*] direction and has a spherical shape. Large changes in E_{hk0} and μ_{hk0} on the [*hkl*] direction indicate a strong anisotropy of the elasticity of disordered cubic titanium monoxide TiO_y with any oxygen content *y*.

The spatial three-dimensional distributions of Young's modulus E_{hkl} and bulk modulus B_{hkl} of disordered cubic titanium monoxides $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ are shown in Figure 2.

Titanium monoxide $TiO_{0.80}$ corresponds to the lower boundary of the homogeneity region and has the lowest values of elastic constants c_{11}, c_{12} and c_{44}, while titanium monoxide $TiO_{1.20}$, which almost reaches the upper boundary of the homogeneity region, has the largest values of c_{11}, c_{12} and c_{44}. For all titanium monoxides, the largest Young's modulus E_{max} is observed in the [00(±1)], [0(±1)0], or [(±1)00] directions. The smallest E_{min} value is observed in eight equivalent directions [(±1)(±1)(±1)]. For titanium monoxides $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$, the largest values of Young's modulus are ~341, ~499 and ~558 GPa, and the smallest are ~67, ~109 and ~125 GPa, respectively [Figure 2(*a*)–(*c*)]. The bulk moduli B_{hkl} of titanium monoxides $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ are ~194, ~217 and ~230 GPa, respectively [Figure 2(*d*)–(*f*)].

From the analysis performed, it follows that disordered cubic titanium monoxide TiO_y is characterized by a pronounced anisotropy of elastic properties throughout the homogeneity region.

Pugh[14] proposed using the ratio of bulk modulus *B* to shear modulus *G* of polycrystalline metals to predict brittle and ductile behavior of materials. Currently, the inverse Pugh ratio $k = G/B$ is used as such a criterion. The critical *G*/*B* ratio separating ductile from brittle substances is 0.57. Thus, substances with $k = G/B < 0.57$ are ductile materials.

The isotropic elastic moduli *G* and *B* of polycrystalline titanium monoxide were calculated by the Voigt–Reuss–Hill method[15] using elastic constants c_{ij}. The inverse Pugh ratio $k = G/B$ throughout the TiO_y homogeneity region varies from ~0.370 to ~0.387, so titanium monoxide can be considered as a ductile material. This is consistent with previously published data[9] that titanium monoxide $TiO_{1.00}$ is characterized by a $k = G/B$ value of 0.382 and is a ductile substance.

In this work, using experimental data on the microhardness of disordered cubic titanium monoxide, the dependences of the shear modulus $G(y)$ and bulk modulus $B(y)$ of titanium monoxide TiO_y are found. For the first time, elastic constants c_{ij} of disordered cubic titanium monoxide TiO_y were estimated as functions of the oxygen content y in the homogeneity region from $TiO_{0.80}$ to $TiO_{1.25}$.

Large changes in the elastic characteristics of TiO_y depending on the [*hkl*] direction indicate a strong anisotropy of the elasticity of disordered cubic titanium monoxide TiO_y.

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