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Strong elasticity anisotropy for disordered cubic titanium monoxide TiO_y

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The elastic constants c_{11}, c_{12}, c_{44} are estimated for the first time as functions of the oxygen content y in the homogeneity region $TiO_{0.80}$–$TiO_{1.25}$ of disordered cubic TiO_y titanium monoxide. The elastic stiffness constants c_{ij} of disordered TiO_y increase with a rise in the relative oxygen content y. The values of elastic moduli depend on the crystallographic $[hkl]$ direction. Large changes in the elastic characteristics of TiO_y depending on the $[hkl]$ direction indicate a strong anisotropy of the elastic properties of disordered TiO_y. Titanium monoxide TiO_y has a much greater anisotropy of elastic properties than the related cubic titanium carbide TiC_y. Disordered TiO_y exhibits mechanical stability over the entire homogeneity region. Based on the ratio of the bulk modulus B and shear modulus G, polycrystalline TiO_y can be considered as a ductile material. The calculated Debye temperature of polycrystalline cubic TiO_y increases non-linearly with a rise in the relative oxygen content y.

Keywords: Elastic constants, nonstoichiometry, elastic properties anisotropy, mechanical stability, Debye temperature.

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1. Introduction

Disordered cubic TiO_y and TiC_y with $B1$ type basis structures are related nonstoichiometric interstitial titanium compounds. The difference between them is caused by structural vacancies (unoccupied by lattice site atoms) present simultaneously in the non-metal and metal sublattices of titanium monoxide, while in titanium carbide, vacancies are only present in the non-metal sublattice [1]. Due to the double faultiness of TiO_y and single faultiness of TiC_y, these compounds, other things being equal, will have different densities of atomic packing that shall result in difference in their anisotropy. Elastic anisotropy analysis of disordered cubic TiC_y in [2] has shown that titanium carbide has weak anisotropy that grows a little with increasing faultiness of the carbon sublattice, but remains negligible even on the lower boundary of its homogeneity region $TiC_{0.50}$. The study will investigate the anisotropy of disordered cubic TiO_y in its homogeneity region.

Cubic (space group $Fm\bar{3}m$) TiO_y with $B1$ type basis structure has one of the widest homogeneity regions (from $TiO_{0.80}$ to $TiO_{1.25}$ at ~ 1273 K) among nonstoichiometric cubic monoxides and monocarbides [1,3–6]. The composition of titanium monoxide with contained structural vacancies in each of the sublattices is written as $Ti_xO_z \equiv TiO_y$ or $Ti_x\blacksquare_{1-x}O_z\square_{1-z} \equiv TiO_y$, where $y = z/x$, $\square$ and $\blacksquare$ are structural vacancies of non-metal (oxygen) and metal (titanium) sublattices, respectively. Titanium monoxide, that formally has a stoichiometric equiatomic composition $TiO_{1.0}$, contains 16.7 at.% of vacancies per titanium and oxygen sublattices, therefore its real composition, including the sublattice faults, is $Ti_{0.833}O_{0.833}$ [3,7].

In disordered state, atoms and structural vacancies are distributed randomly over the sites of each of Ti_xO_z sublattices, but the cubic symmetry of each sublattice is maintained, because the probability of detecting an atom on all sites of its own sublattice is the same and coincides with the relative content of occupied sublattice sites, i.e. is equal to x for the titanium sublattice and to z for the oxygen sublattice.

Depending on the content of oxygen and thermal treatment conditions, distribution of atoms and vacancies in the crystal lattice of TiO_y may be disordered or ordered. Disordered condition of titanium monoxide is thermodynamically stable at $T > 1600$ K, while several ordered phases of different types and symmetries occur at a temperature below 1500 K in different concentration and temperature ranges [1,8,9]. A monoclinic (sp. gr. $C2/m$) phase $Ti_5\blacksquare O_5\square$ is the main ordered phase of nonstoichiometric cubictitanium titanium monoxide.

All properties of titanium monoxide depend on a relative oxygen content and vary significantly within its homogeneity range. Lattice constant of disordered cubic TiO_y decreases smoothly with the growth of the relative oxygen content y [8] According to [6,10–13], all disordered titanium monoxides have low specific resistance. Depending on the oxygen content, the specific resistance of disordered TiO_y with $y \leq 1.0$ slowly grows with temperature, and decreases when $y > 1.0$; thus, TiO_y have electronic conductivity with low oxygen content $y \leq 1.0$ and behave as narrow-gap semiconductors or insulators at a higher oxygen content $y > 1.0$. Specific heat capacity of disordered nonstoichiometric TiO_y $(0.81 \leq y \leq 1.26)$ grows with relative oxygen content y throughout the homogeneity region of the cubic phase [14].

Table 1. Theoretical elastic constants c_{ij}, bulk modulus B and shear modulus G of equiatomic quasi-stoichiometric $TiO_{1.00}$

c_{11}, GPa	c_{12}, GPa	c_{44}, GPa	B, GPa	G, GPa	Approximation	Ref.
693	73	130	280	–	LDA	16
517.2	71.3	36.2	220.0	222.5	GGA	17
650	72	145	270	–	TBPM*	18
612	129	123	249.8	241.5	LDA	19
511	53	31	205	78	GGA	20

* three-body potential model.

Data on the stress-strain properties of cubic titanium monoxide are limited by microhardness measurements on quenched TiO_y samples within $0.92 \le y \le 1.26$ [15], where nonlinear microhardness growth is observed as y increases.

Utilization of disordered titanium monoxide is associated with its stress-strain properties. Variation of the titanium monoxide nonstoichiometry is one of the ways to control elastic properties. However, no experimental data on the elastic properties of disordered cubic TiO_y depending on the oxygen content are reported in the literature.

Theoretical calculations of elastic response are reported only for equiatomic quasi-stoichiometric $TiO_{1.00}$. Theoretical estimates of the elastic properties have been generally made in different density functional theory (DFT) versions with local density approximation (LDA) and generalized gradient approximation (GGA) for exchange-correlation potentials at 0 K. Elastic stiffness constants c_{ij} and elastic moduli of equiatomic quasi-stoichiometric $TiO_{1.00}$ calculated in [16–20] are listed in Table 1.

Ab initio calculations by the DFT method were used in [20] to study, besides cubic (sp. gr. $Fm\bar{3}m$) equiatomic TiO, the elastic anisotropy of TiO_2, Ti_2O_3, Ti_3O and Ti_3O_5. According to [20], cubic TiO has the highest elastic anisotropy compared with other examined titanium oxides.

According to the theoretical data in [16–20], cubic TiO has highly pronounced elastic anisotropy.

The elastic stiffness constant matrix of cubic crystals includes 3 independent elastic constants — c_{11}, c_{12} and c_{44}, and the elastic compliance constant matrix s_{ij} includes three constant: s_{11}, s_{12} and s_{44}. To consider the elastic anisotropy of nonstoichiometric cubic TiO_y, it is important to know how elastic constants c_{11}, c_{12} and c_{44} or s_{11}, s_{12} and s_{44} vary depending on the relative oxygen content y. Therefore, the experimental microhardness data reported in [15] for disordered nonstoichiometric TiO_y with different oxygen content will be used herein for quantitative analysis of the elastic constants of nonstoichiometric TiO_y and for elastic anisotropy estimation. To compare the elastic anisotropy of disordered TiO_y, related disordered cubic TiC_y will be used.

2. Findings and discussion

2.1. Elastic constants of titanium monoxide

Hardness study of carbides, nitrides and other compounds [21] has identified a general downward trend of their hardness H_V as the shear modulus G and uniform compression modulus B decrease. According to [21,22], the dependence of microhardness on shear modulus for nonstoichiometric compounds is written as $H_V(y) = 0.151G(y)$. This function allows the shear modulus $G(y)$ to be found depending on the composition of disordered TiO_y according to the data reported in [15] on its microhardness variation as

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

The quantitative analysis has shown that the shear modulus$G_{y=1}$ of stoichiometric $TiO_{1.00}$ is equal to 77.4 GPa, and the concentration dependence $G(y)$ of disordered TiO_y is written as

$$G(y) = G_{y=1}(-3.23902 + 7.17183y - 2.93282y^2) \pm 10.0\,\text{GPa}. \quad (2)$$

The concentration dependences of microhardness $H_V(y)$ and shear modulus $G(y)$ of disordered TiO_y allow the concentration dependence of bulk modulus $B(y)$ to be found using the empiric function $H_V = [2(k^2G)^{0.585}-3]$ proposed in [23]. It follows from this function that

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

Dependence of the bulk modulus B of disordered TiO_y calculated using relation (3) from $H_V(y)$ of quenched TiO microhardness [15] using the found quantitative dependence $G(y)$ (2) is written as

$$B(y) = B_{y=1}(-2.60339 + 6.11632y - 2.51292y^2) \pm 10.0\,\text{GPa}. \quad (4)$$

According to the calculation, the bulk modulus $B_{y=1}$ of stoichiometric $TiO_{1.00}$ is equal to 123.8 GPa.

To pass from the found quantitative dependences of $G(y)$ and $B(y)$ of titanium monoxide to its elastic stiffness constants c_{11}, c_{12} and c_{44}, an approach is further used as proposed and developed in [22] for nonstoichiometry and elastic properties of cubic TiC_y.

The bulk modulus of isotropic cubic crystals is correlated to the elastic stiffness constants through a simple relation $B = (c_{11} + 2c_{12})/3$ [24,25]. To a first approximation, dependence $B(y)$ of TiO_y single-crystal particles on the relative oxygen content y is the same as $B(y)$ (4) found using the experimental data [15] on microhardness $H_V(y)$. Therefore,

$$(c_{11}+2c_{12})/3 = B_{y=1}(-2.60339+6.11632y-2.51292y^2).$$

Table 2. Elastic stiffness constants c_{ij} elastic compliance constants s_{ij} and elastic anisotropy criterium A_{an} of disordered cubic TiO_y

y	c_{11}, GPa	c_{12}, GPa	c_{44}, GPa	s_{11}, Pa^{-1}	s_{12}, Pa^{-1}	s_{44}, Pa^{-14}	A_{an}
0.80	348.2	36.1	19.3	$2.929 \cdot 10^{-12}$	$-0.275 \cdot 10^{-12}$	$51.91 \cdot 10^{-12}$	0.124
0.85	398.5	41.3	22.9	$2.559 \cdot 10^{-12}$	$-0.240 \cdot 10^{-12}$	$43.71 \cdot 10^{-12}$	0.128
0.90	442.4	45.9	26.0	$2.305 \cdot 10^{-12}$	$-0.217 \cdot 10^{-12}$	$38.40 \cdot 10^{-12}$	0.131
0.95	479.9	49.8	28.7	$2.125 \cdot 10^{-12}$	$-0.200 \cdot 10^{-12}$	$34.79 \cdot 10^{-12}$	0.134
1.00	511.0	53.0	31.0	$1.996 \cdot 10^{-12}$	$-0.188 \cdot 10^{-12}$	$32.26 \cdot 10^{-12}$	0.135
1.05	535.7	55.6	32.8	$1.904 \cdot 10^{-12}$	$-0.179 \cdot 10^{-12}$	$30.49 \cdot 10^{-12}$	0.137
1.10	553.9	57.4	34.1	$1.841 \cdot 10^{-12}$	$-0.173 \cdot 10^{-12}$	$29.29 \cdot 10^{-12}$	0.138
1.15	565.7	58.7	35.0	$1.803 \cdot 10^{-12}$	$-0.169 \cdot 10^{-12}$	$28.55 \cdot 10^{-12}$	0.138
1.20	571.1	59.2	35.5	$1.786 \cdot 10^{-12}$	$-0.168 \cdot 10^{-12}$	$28.20 \cdot 10^{-12}$	0.139
1.25	570.1	59.1	35.4	$1.789 \cdot 10^{-12}$	$-0.168 \cdot 10^{-12}$	$28.22 \cdot 10^{-12}$	0.139

Comparison of moduli B and G of quasi-stoichiometric $TiO_{1.00}$ theoretically calculated in [16–20] with $G_{y=1} = 77.4$ GPa and $B_{y=1} = 123.8$ GPa found herein shows that the theoretical values of $G_{calc,y=1} = 78$ GPa and $B_{calc,y=1} = 205$ GPa of quasi-stoichiometric $TiO_{1.00}$ calculated in [20] are the nearest to our estimated values$G_{y=1}$ and $B_{y=1}$. Considering the data [20] on elastic moduli $B_{calc,y=1} = 205$ GPa and $G_{calc,y=1} = 78$ GPa and elastic constants $c_{11} = 511$, $c_{12} = 53$ and $c_{44} = 31$ GPa of equiatomic stoichiometric titanium monoxide, the following relations may be established between the theoretical elastic constants $c_{ij}(y = 1)$ and theoretical bulk and shear moduli of stoichiometric $TiO_{1.00}$ as reported in [20]

$$c_{11}(y = 1) = 2.49268B_{calc,y=1},$$

$$c_{12}(y = 1) = 0.25854_{calc,y=1}$$

and

$$c_{44}(y = 1) = 0.39744G_{calc,y=1}.$$

Disordered cubic TiC_yhas been previously used [2,22] to illustrated that dependences of elastic constants c_{11} and c_{12} on the composition of the nonstoichiometric compound are qualitatively identical. In view of this, $c_{11}(y)$ and $c_{12}(y)$ as functions of the composition of disordered TiO_y are written as

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

$$c_{12}(y) = c_{12}(y = 1)(-2.60339 + 6.11632y - 2.51292y^2), \quad (5b)$$

where $c_{11}(y = 1) = 511$ GPa and $c_{12}(y = 1) = 53$ GPa.

According to [26], the shear modulus of isotropic cubic crystals is correlated to c_{44} as $G = c_{44}$. It is reported in [16] that cubic crystal resistance to shear distortions is more accurately characterized by two moduli: c_{44} and $c' = (c_{11}-c_{12})/2$. c_{44} is related to orthorhombic strain, while c' is related to tetragonal strain. The calculated variation of $G(y)$ (2) from TiO_y composition is the averaged concentration dependence of the shear modulus, because it has been obtained using the dependence $H_V(y)$ of TiO_ymicrohardness [15] measured on polycrystalline titanium monoxide samples. Therefore, $G_{y=1} = c_{44}(y = 1)$ and $c_{44}(y)$ of TiO_y single-crystal particles on the oxygen content y as function of the composition of disordered TiO_y is written as

$$c_{44}(y) = c_{44}(y=1)(-3.23902+7.17183y-2.93282y^2), \quad (5c)$$

where $c_{44}(y = 1) = 31$ GPa.

c_{ij} are directly related to the mechanical stability of the given phase. The phase is generally mechanically stable, if it satisfies Born's criteria reported in [24,27] and the necessary and sufficient conditions of elastic stability of different crystal systems described in [28,29]. The general necessary and sufficient stability criterium is in the fact that all eigenvalues of the elastic stiffness constant matrix shall be positive. The elastic matrix of cubic crystals includes a total of 3 independent positive elastic stiffness constants c_{11}, c_{12} and c_{44}, and the mechanical stability conditions of cubic crystals are written simply as

$$c_{11} > c_{12}, \quad c_{44} > 0, \quad c_{11} + 2c_{12} > 0. \quad (6)$$

Relations between c_{11}, c_{12}, c_{44} and s_{11}, s_{12}, s_{44} of cubic crystals [25] are described as

$$s_{11} = (c_{11} + c_{12})/[(c_{11} - c_{12})(c_{11} + 2c_{12})],$$

$$s_{12} = -c_{12}/[(c_{11} - c_{12})(c_{11} + 2c_{12})], \; s_{44} = 1/c_{44}. \quad (7)$$

c_{ij} and s_{ij} of disordered cubic TiO_y with different compositions as estimated using (5) and (7) are listed in Table 2. It is apparent that mechanical stability condition (6) is satisfied for disordered cubic TiO_y in its homogeneity region.

2.2. Elastic anisotropy of disordered cubic TiO_y

According to the elasticity theory, cubic crystals have elastic anisotropy. In particular, [30] reports the dependences of Young's modulus E_{hkl}, Poison's ratio μ_{hkl} and shear modulus G_{hkl} of cubic crystals on crystallographic direction $[hkl]$ that show their anisotropy. These elastic properties of cubic crystals considering the anisotropy factor Γ are functions of c_{11}, c_{12} and c_{44} and are written as [30]:

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

$$\mu_{hkl} = 1/2 - \frac{E_{hkl}}{2(c_{11} + 2c_{12})}, \quad (9)$$

$$G_{hkl} = \frac{2(c_{11} - c_{12})c_{44}}{4c_{44} - 6(2_{44} - c_{11} + c_{12})\Gamma}. \quad (10)$$

In equations (8)–(10), Γ is an anisotropy factor of cubic crystals equal to

$$\Gamma = \frac{h^2k^2 + h^2l^2 + k^2l^2}{(h^2 + k^2 + l^2)^2} \text{ [30].}$$

The bulk modulus B of cubic crystals does not depend on direction $[hkl]$ and is equal to

$$B = (c_{11} + 2c_{12})/3. \quad (11)$$

The calculated $c_{ij}(y)$ (5) of disordered cubic TiO_y and quantitative data on c_{11}, c_{12}, c_{44} and s_{11}, s_{12}, s_{44} of titanium monoxide with different relative oxygen content y (see Table 2) were used for calculation using equations (8)–(11) for distribution of elastic properties of single-crystal cubic TiO_y depending on direction $[hkl]$ and relative oxygen content y. Figure 1 shows the plotted distributions of Young's modulus $E_{hkl}(y)$ and shear modulus $G_{hkl}(y)$ in (100) plane of cubic TiO_y with different relative oxygen contents y. Poison's ratio $\mu_{hkl}(y)$ of titanium monoxide depends only tenuously on y, therefore, its distribution is shown only for $y = 0.8$ and 1.0 (see Figure 1). Due to cubic symmetry of titanium monoxide, distributions of its elastic properties $E_{hkl}(y)$, $G_{hkl}(y)$ and $\mu_{hkl}(y)$ in (010) and (001) planes are the same as in (100) plane.

Young's modulus E_{hk0} of $TiO_{0.80}$ corresponding to the lower boundary of the homogeneity region of the disordered cubic phase in (100) plane varies from ~ 341 to ~ 70 GPa. For equiatomic $TiO_{1.00}$, Young's modulus varies from ~ 499 to ~ 111 GPa and for $TiO_{1.20}$ — from ~ 558 to ~ 128 GPa (Figure 1). The maximum and minimum values of G_{hk0} vary from ~ 156 to ~ 25 GPa for $TiO_{0.80}$, from ~ 229 to ~ 39 GPa for equiatomic $TiO_{1.00}$ and from ~ 256 to ~ 45 GPa for $TiO_{1.20}$ (see Figure 1). Poison's ratio μ in (100) plane of titanium monoxides depending on direction $[hkl]$ varies from ~ 0.094 to ~ 0.417 and almost does not depend on the composition of TiO_y (see Figure 1). Bulk modulus B of cubic titanium monoxide does not depend on direction $[hkl]$ and has a spherical shape, B of $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ is equal to ~ 194, ~ 217 and ~ 230 GPa, respectively. Large changes of E_{hk0}, G_{hk0} and μ_{hk0} from direction $[hkl]$ indicate high elastic anisotropy of disordered cubic TiO_y with any relative oxygen content y in its homogeneity region.

Spatial 3D distributions of E_{hkl} and B_{hkl} of disordered cubic $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ with different relative oxygen content y are shown in Figure 2. $TiO_{0.80}$ corresponds to the lower boundary of the homogeneity region and has the lowest c_{11}, c_{12} and c_{44}, and $TiO_{1.20}$ composition almost achieves the upper boundary of the homogeneity region and is distinguished by the highest values of c_{11}, c_{12} and c_{44} (see Table 2). Equiatomic $TiO_{1.00}$ occupies an intermediate position between $TiO_{0.80}$ and $TiO_{1.20}$. For all titanium monoxides, the highest $E_{\max}$ is observed along one of the crystallographic axes $[00 \pm 1]$, $[0 \pm 10]$ or $[\pm 100]$. The lowest $E_{\min}$ is observed in eight equivalent directions $[\pm 1 \pm 1 \pm 1]$. The highest and lowest Young's moduli of $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ are equal to ~ 341 and ~ 67, ~ 499 and ~ 109, ~ 558 and ~ 125 GPa, respectively (see Figure 2, *a*). Values of B_{hkl} of $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ are equal to ~ 194, ~ 217 and ~ 230 GPa, respectively, B_{hkl} have spherical shape and do not depend on direction $[hkl]$ (see Figure 2, *b*).

For comparison, Figure 3 shows the spatial 3D distributions of E_{hkl} of disordered cubic $TiC_{0.50}$ and $TiC_{1.00}$corresponding to the lower and upper boundaries of the homogeneity regions of titanium carbide calculated in [22]. According to [22], the highest and lowest Young's moduli for nonstoichiometric $TiC_{0.50}$ are equal to $E_{\max} = 440$ GPa and $E_{\min} = 346$ GPa, while $E_{\max}$ and $E_{\min}$ for stoichiometric $TiC_{1.00}$ are equal to 477 and 450 GPa, respectively. Thus, $E_{\max}$ and $E_{\min}$ of TiC_y are little different from each other compared with $E_{\max}$ and $E_{\min}$ of TiO_y. Therefore, TiO_y has a much higher elastic anisotropy than the related cubic TiC_y.

The analysis of variation of elastic properties depending on the composition of TiO_y generally suggests that disordered cubic titanium monoxide shows strong anisotropy throughout the homogeneity region.

Anisotropy may be estimated using the ratio of the lowest and highest Young's moduli, i.e. $E_{\min}/E_{\max}$. For $TiO_{0.80}$ and $TiO_{1.25}$ corresponding to the lower and upper boundaries of the homogeneity region, this ratio is equal to 0.205 and 0.227, respectively, i.e. $E_{\min}$ and $E_{\max}$ differ almost by a factor of 5. For $TiC_{0.50}$ and $TiC_{1.00}$, $E_{\min}/E_{\max}$ are equal to 0.786 and 0.943, i.e. are very little different. This comparison also confirms very strong elastic anisotropy of TiO_y and very weak elastic anisotropy of TiC_y.

For quantitative description of the elastic anisotropy of cubic crystals, [31] offers a simple criterium $A_{\text{an}} = 2c_{44}/(c_{11} - c_{12})$ that is equal to 1 for isotropic cubic crystals. According to [31], the lower A_{an} the higher elastic anisotropy. The calculated anisotropy criterion A_{an} of cubic TiO_y varies from 0.124 to 0.139 for monoxides from $TiO_{0.80}$ to $TiO_{1.25}$ (see Table 2). This indicates very high elastic anisotropy of cubic titanium monoxide that is a little

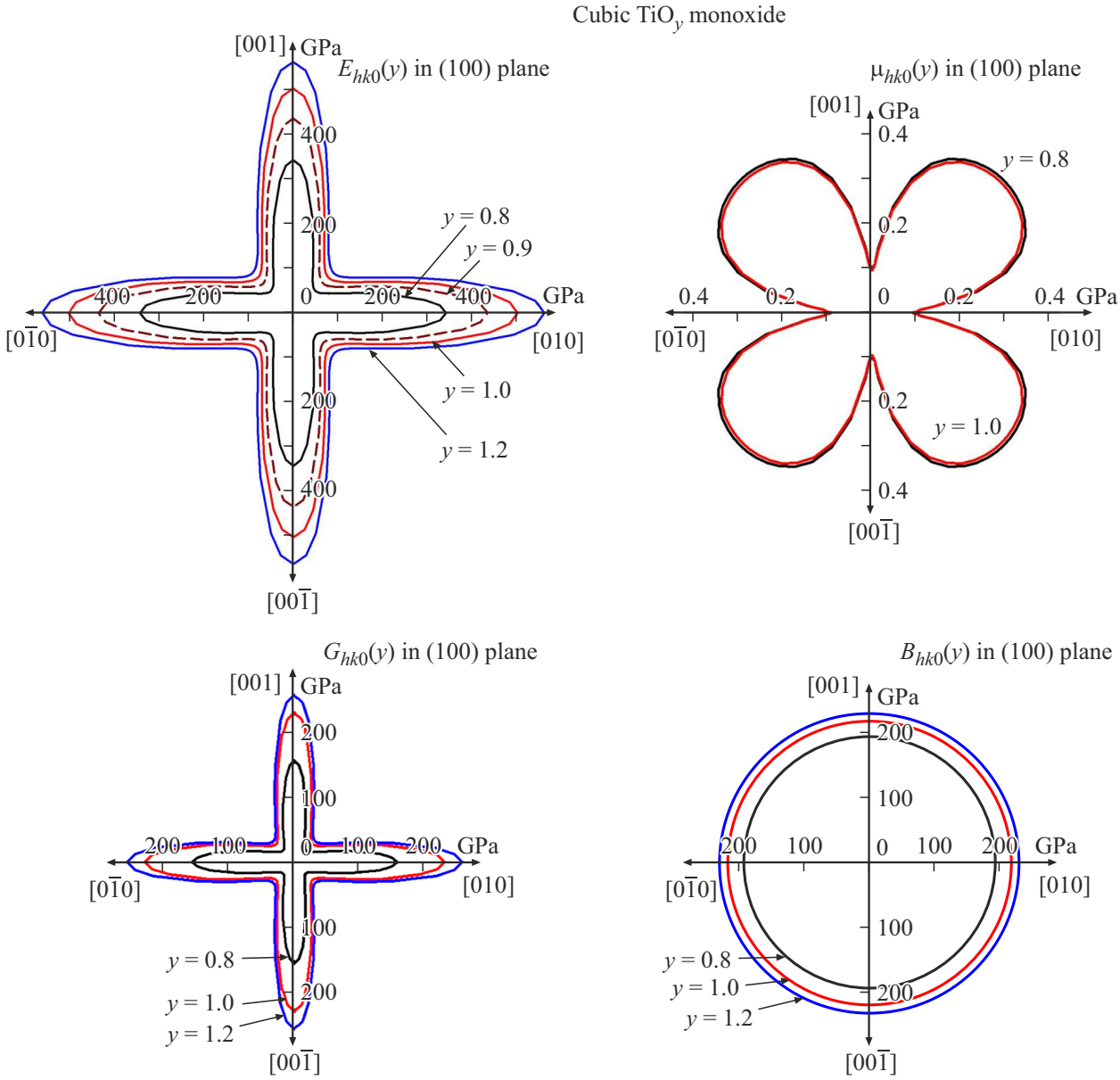

Figure 1. Dependences of Young's modulus E ($y = 0.8$, 0.9, 1.0 and 1.2), Poison's ratio μ ($y = 0.8$ and 1.0), shear modulus G ($y = 0.8$, 1.0 and 1.2) and bulk modulus B ($y = 0.8$, 1.0 and 1.2) on crystallographic direction $[hkl]$ in (100) plane of cubic TiO_y with different relative oxygen content y.

weakened with the growth of y in TiO_y. Such conclusion agrees with the conclusion on strong anisotropy made according to the variation of elastic properties depending on the composition of disordered cubic TiO_y in its homogeneity region. A_{an} of the related cubic titanium carbide varies from ~ 0.68 to ~ 0.91 for carbides from $TiC_{0.50}$ to $TiC_{1.00}$ [22] that indicates low elastic anisotropy TiC_y compared with TiO_y. Anisotropy of crystals is generally caused by different densities of atomic packing in crystal lattice of a compound in different directions. Vacancies present in metal and oxygen sublattices of TiO_y cause a much higher difference in densities of atomic packing in TiO_y compared with TiC_y where vacancies are only present in non-metal sublattice. This results in much higher elastic anisotropy of titanium monoxide compared with titanium carbide.

3. Plasticity and Debye temperature of TiO_y

In [32], it is proposed to use the ratio of B and G of polycrystalline metals to forecast brittle fracture and plastic behavior of materials. According to the estimations made for metals, oxides, carbides, nitrides and other compounds, $B/G > 1.75$ correspond to ductile materials,

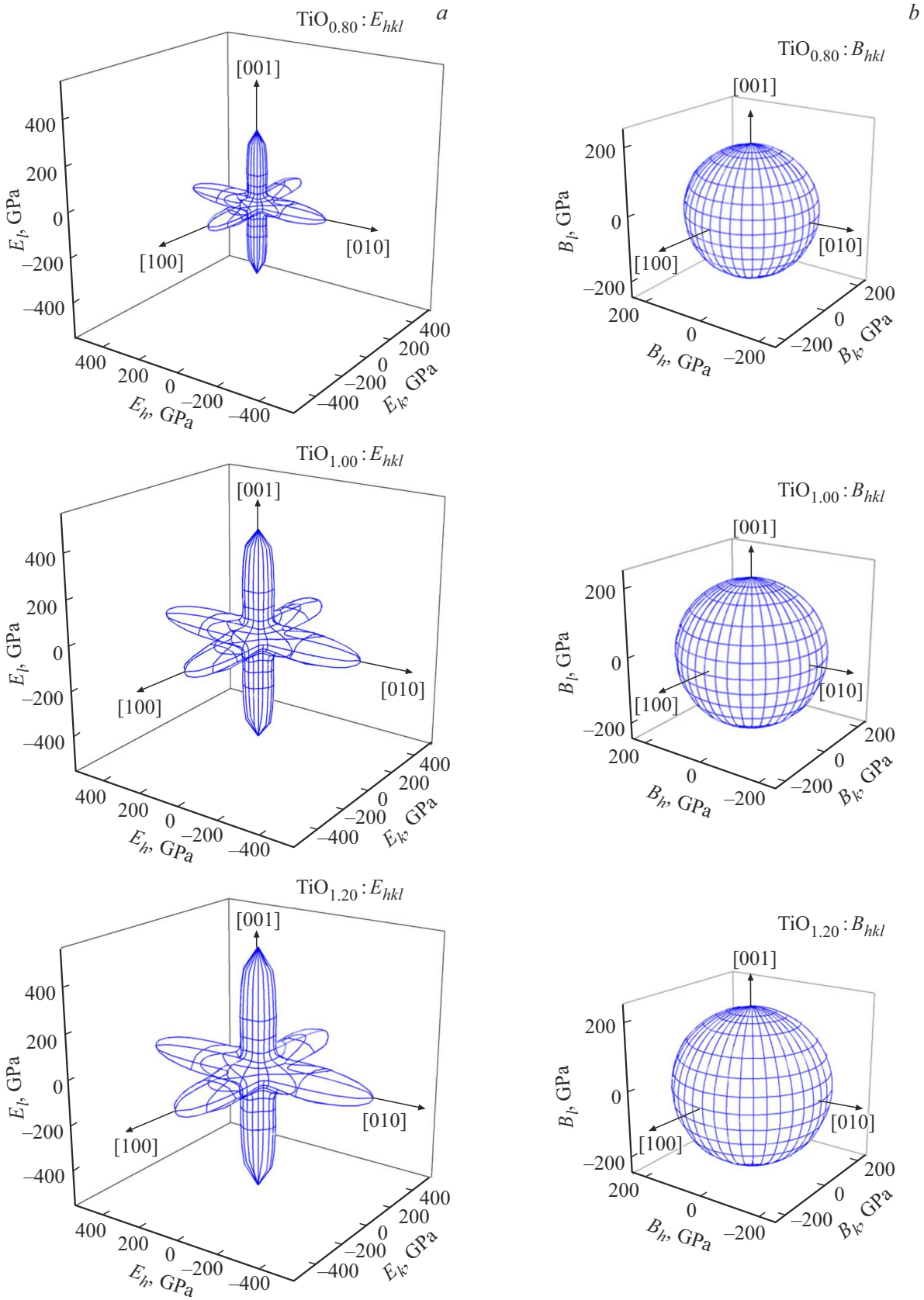

Figure 2. The calculated spatial distributions *a*) of E_{hkl} and of *b*) B_{hkl} of disordered cubic $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.20}$ with different relative oxygen content *y*.

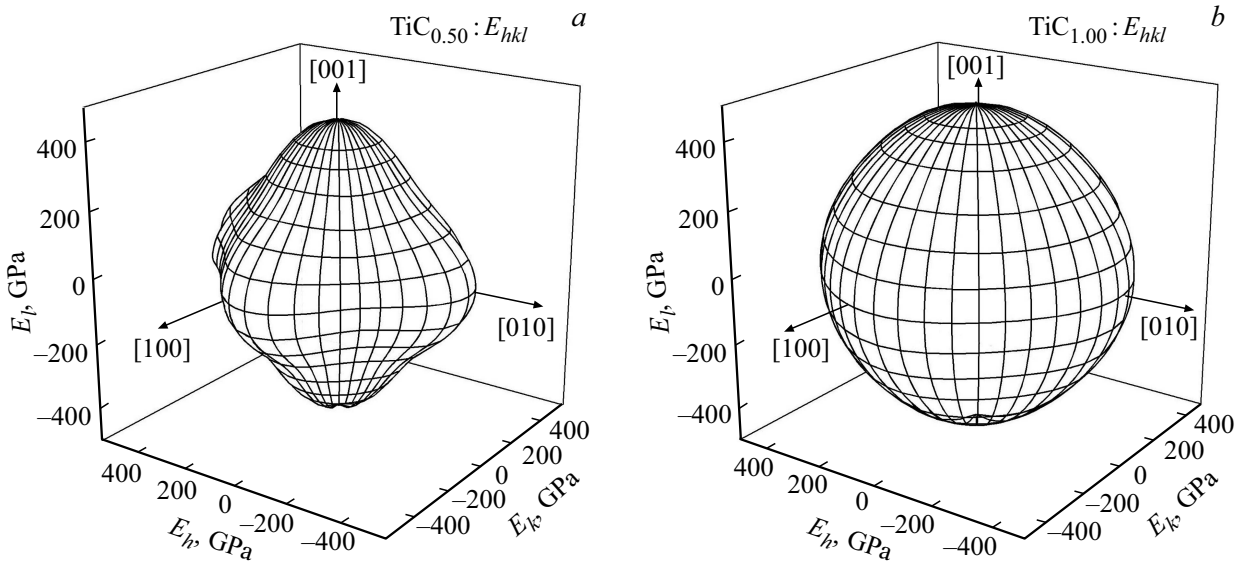

Figure 3. Spatial distributions of E_{hkl} of cubic $TiC_{0.50}$ and $TiC_{1.00}$ [22].

while $B/G < 1.75$ are inherent in brittle materials. Inverse ratio is currently used: $k = G/B$. Critical value of G/B, that separates ductile substances from brittle ones, is equal to approx. 0.57, i. e. substances with $k = G/B < 0.57$ are ductile.

Isotropic elastic moduli of polycrystalline materials were calculated by the method reported in [33] using elastic stiffness constants c_{ij} and elastic compliance constants s_{ij} (see Table 2). B and G of polycrystalline $TiO_{0.80}$, $TiO_{1.00}$ and $TiO_{1.25}$ (Table 3) calculated by method [33] are equal to 140.1 and 51.8, 205.7 and 78.8, 229.4 and 88.8 GPa, respectively. Considering this, B/G of TiO_y throughout the homogeneity region is high and varies from 2.70 to 2.58, while $k = G/B$ varies from ~ 0.370 to ~ 0.387, therefore, titanium monoxide may be treated as a ductile material. This agrees with [20] where $k = G/B$ of $TiO_{1.00}$ is equal to 0.382, and $TiO_{1.00}$ is reported as a wrought ductile substance.

Distribution of elastic oscillations in a solid body depends on its elastic properties. longitudinal speed of sound v_L and transverse speed of sound v_t in an isotropic polycrystalline substance may be calculated using its B and G by a mean type method [33]. According to [34], longitudinal speed of sound v_L, transverse speed of sound v_t and mean speed of sound v_m are written as

$$v_L = \sqrt{(3B + 4G)/3\rho}\,[\mathrm{m \cdot s^{-1}}], \tag{12a}$$

$$v_t = \sqrt{G/\rho}\,[\mathrm{m \cdot s^{-1}}], \tag{12b}$$

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_L^3}\right)\right]^{-1/3} [\mathrm{m \cdot s^{-1}}]. \tag{12c}$$

The Debye temperature θ_D may be calculated using the mean elastic oscillation propagation velocity (mean speed of sound) v_m (12 s) that depends directly on B and G. According to [34], dependences of θ_D on v_m is written as

$$\theta_D = \frac{h}{k_B}\left(\frac{3nN_A\rho}{4\pi M}\right)^{1/3} v_m,\ [\mathrm{K}], \tag{13}$$

where $h = 6.6262 \cdot 10^{-34}\,\mathrm{J \cdot sec}$ is Planck's constant. $k_B = 1.3807 \cdot 10^{-23}\,\mathrm{J \cdot K^{-1}}$ is Boltzmann constant $N_A = 6.022 \cdot 10^{23}\,\mathrm{mol^{-1}}$ is Avogadro's number, ρ is the density, M is the molecular weight, n is the number of atoms per a formula unit of the compound. Is the molecular weight of $Ti_xO_z \equiv TiO_y$ considering content of

Table 3. Calculated Young's modulus E, bulk modulus B and shear modulus G and direct ductility criterium B/G and inverse ductility criterium $k = G/B$ of polycrystalline TiO_y

y	E_V, GPa	E_R, GPa	E, GPa	G_V, GPa	G_R, GPa	G, GPa	B, GPa	B/G	$k=G/B$
0.80	188.7	76.5	132.6	74.0	29.7	51.8	140.1	2.704	0.370
0.85	217.1	90.7	153.9	85.2	35.1	60.1	160.4	2.667	0.375
0.90	241.8	103.1	172.5	94.9	39.9	67.4	178.1	2.641	0.378
0.95	263.0	113.8	188.4	103.2	44.0	73.6	193.2	2.623	0.381
1.00	280.5	122.6	201.6	110.2	47.4	78.8	205.7	2.610	0.383
1.05	294.4	129.6	212.0	115.7	50.1	82.9	215.6	2.601	0.385
1.10	304.7	134.9	219.8	119.8	52.1	85.9	222.9	2.594	0.385
1.15	311.4	138.4	224.9	122.4	53.5	87.9	227.7	2.589	0.386
1.20	314.5	140.1	227.3	123.6	54.1	88.9	229.9	2.586	0.387
1.25	314.0	140.0	227.0	123.5	54.1	88.8	229.4	2.585	0.387

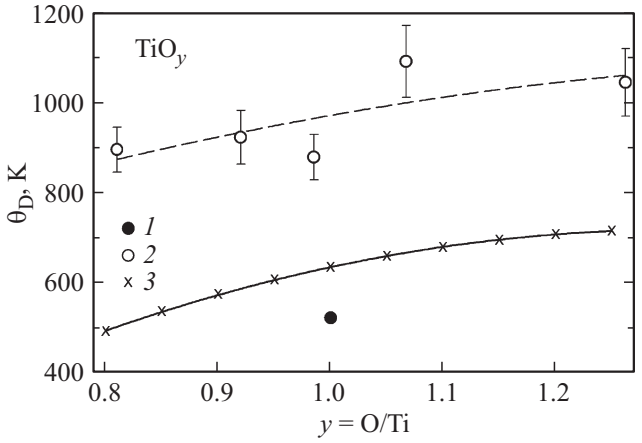

Figure 4. Variation of the Debye temperature θ_D depending on the composition of polycrystalline disordered cubic TiO_y: *1* — data of [19], *2* — data of [14], *3* — calculation of θ_D herein.

vacancies in the titanium and oxygen sublattices is equal to $M = xA_{Ti} + zA_O$.

Using the calculated isotropic B and G of polycrystalline TiO_y (see Table 3) and ρ of TiO_y measured in [35], we have calculated the speeds of sound and Debye temperature θ_D depending on the composition of polycrystalline TiO_y (Figure 4).

The calculated θ_D increase from ~ 490 K for $TiO_{0.80}$ to ~ 715 K for $TiO_{1.25}$. According to the theoretical estimation [19], the Debye temperature of equiatomic $TiO_{1.00}$ is equal to ~ 521 K and is quite close to the calculated value $\theta_D = 603$ K. The Debye temperature of cubic TiO_y $(0.81 \le y \le 1.26)$ have been previously estimated using the experimental heat capacity measurements within 340−600 K [14]. θ_D values calculated by us are about 65% of the experimentally estimated θ_D of disordered cubic TiO_y from temperature dependences of heat capacity $C_p(T)$ [14]. Higher θ_D values estimated in [14] are probably caused by the use of $C_p(T)$ measured at $T > 300$ K. The elastic properties used herein for the Debye temperature estimation correspond to 0 K.

4. Conclusion

The paper has for the first time estimated the elastic constants c_{ij} and s_{ij} depending on the oxygen content y in the homogeneity region $TiO_{0.80}$−$TiO_{1.25}$ of disordered TiO_y. Disordered cubic titanium monoxide is mechanically stable and features strong anisotropy throughout the homogeneity region. By the ratio of the bulk modulus B and shear modulus G, titanium monoxide may be treated as a ductile material.

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Conflict of interest

The authors declare that they have no conflict of interest.

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