Elasticity and Anisotropy of Titanium Oxide Ti_xO_y

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Abstract. The elastic properties and their anisotropies of Ti_xO_y (TiO，TiO_2，Ti_2O_3, Ti_3O, Ti_3O_5) were investigated based on first-principles calculations with the generalized gradient approximation (GGA) . The elastic constants and modulus, Poisson's ratio and universal anisotropic index were obtained. The bonds properties of the five materials were analyzed through Poisson's ratio and Pugh modulus ratio (G/B). The five titanium oxides are elastically anisotropic. Details of anisotropies were demonstrated in 3D plots.

Keywords： Titanium Oxide; first-principles; elasticity; anisotropy

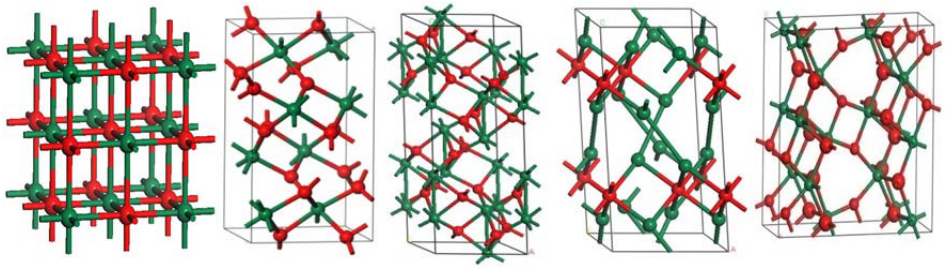
1 Introduction

Titanium dioxide (TiO_2) is one of the best known wide band gap semiconductors with many unique properties like excellent photo activity, long-term stability, low cost and non-toxicity, which make it become the most common uses for photo catalytic material. A number of experimental and theoretical studies indicate that TiO_2 has many polymorphs, such as rutile (P42/mnm), anatase (I41/amd) and brookite (Pbca) [1-3]. However, lots of researches focus on titanium dioxide, but the discussions of other titanium oxides are less. In this paper, the elastic properties and their anisotropies of Ti_xO_y (TiO, TiO_2, Ti_2O_3, Ti_3O, Ti_3O_5) are investigated, which is significant to the practical application of titanium oxide.

2 Calculation Methods and Theory

2.1 Calculation parameter and model

The crystal structure of five titanium oxides (TiO，TiO_2，Ti_2O_3，Ti_3O，Ti_3O_5) are shown in Figure 1. The first principles calculation based on DFT [4] was used with the aid of the CASTEP [5] program. The exchange and correlation potentials were Perdew-Burke-Ernzerhof method based on generalized gradient approximation (GGA) [6]. The crystal wave function was expanded by the plane wave basis set, and the interaction potential for ion core and valence electron was determined based on the ultrasoft pseudopotential [7].



(a) (b) (c) (d) (e)

Figure 1. The crystal Structures of the five Ti_xO_y. The small green spheres and red spheres denote Ti and O atoms, respectively. (a) TiO (Fm3m), (b) Brookite of TiO_2 (Pbca), (c) Ti_2O_3 (R-3C), (d) Ti_3O (P-31c), (e) Anosovite of Ti_3O_5 (Cmcm).

2.2 Elastic properties and their anisotropies

To calculate the bulk modulus and shear modulus, we refer to the models of Voigt and Reuss, respectively. The bulk modulus and shear modulus for monoclinic structure are given by [8]:

$$B_V = (1/9)[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] \quad (1)$$

$$G_V = (1/15)[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})] \quad (2)$$

$$B_R = [(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})]^{-1} \quad (3)$$

$$B_R = (1/15)[4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})]^{-1} \quad (4)$$

Based on extreme value principle, Hill [9] has proved that Voigt's and Reuss's models are the upper and lower limits of the elastic constant, respectively. The arithmetic mean Voigt–Reuss–Hill (VRH) value is closer to the experimental result.

$$B = (B_V + B_R)/2, \quad G = (G_V + G_R)/2 \quad (5)$$

Using Hill's value of bulk modulus and shear modulus, the Young's modulus and Poisson's ratio for each material under polycrystalline system were obtained:

$$E = (9BG)/(3B + G), \quad \nu = \frac{3B - 2G}{2(3B + G)} \quad (6)$$

To conduct quantitative research on the anisotropy of a single crystal, we calculated the universal anisotropic index A^U [10] which describes the anisotropy of elasticity for single crystals.

$$A^U = 5G_V / G_R + B_V / B_R - 6 \geq 0 \quad (7)$$

Here A^U =0 refers to a locally isotropic single crystal. Any departure from zero corresponds to a degree of elastic anisotropy possessed by the crystal.

3 Calculation Results and Discussion

3.1 Structural parameters

We used GGA method obtained the structural parameters of the five Ti_xO_y, and the results of geometric parameters after optimization list in Table 1. From table 1, it can be seen that the parameters of five titanium oxides are different. The calculations suggest that the density of Ti_2O_3 is the largest among these five materials while Ti_3O_5 is opposite.

TABLE 1. THE CALCULATED LATTICE PARAMETERS，VOLUME PER FORMULA AND DENSITIES FOR FIVE TITANIUM OXIDES USING GGA(GENERALIZED GRADIENT APPROXIMATION).TI_XO_Y STRUCTURE CONSTANTS *A*, *B, C*[Å], VOLUME *V*[$Å^3$], AND DENSITY *P*[$G.CM^{-3}$]

name	TiO	TiO_2	Ti_2O_3	Ti_3O	Ti_3O_5
Space group	Fm3m	Pbca	R-3C	P-31c	Cmcm
a	4.29	9.28	5.13	5.17	3.74
b	4.29	5.52	5.13	5.17	10.08
c	4.29	5.19	14.16	9.52	10.17
V	79.23	265.66	322.79	220.35	383.62
$\rho(g/cm^3)$	5.38	4.01	5.45	4.84	3.90

3.2 Elastic properties and their anisotropies

Elastic constants characterize the reaction of crystal lattice to external stress within the elastic limit. Table 2 shows the elastic constants and elastic modulus of these five titanium oxides.

Some parameters for polycrystals, bulk modulus *B*, shear modulus *G*, Young's modulus *E*, Pugh modulus ratio *G/B*, and Poisson's ratio are listed in Table 2. According to Pugh's criterion [11], materials with Pugh modulus ratio $G/B > 0.57$ show brittleness, whereas materials with $G/B < 0.57$ show ductility. The results of *G/B* in Table 2 indicate that the former materials (TiO, TiO_2, Ti_2O_3 and Ti_3O) show ductility, and the sequence of *G/B* is $Ti_2O3(0.498) > Ti_3O(0.457) > TiO2(0.443) > TiO(0.382)$, indicating that Ti_2O3 possesses the highest directing property of bonds, TiO conversely possesses the lowest directing property of bonds. The result of *G/B* for Ti_3O5 equals to 0.718, indicating that Ti_3O5 can be classified as brittle material. Moreover, the lowest *G/B* value of TiO in calculations indicates that it has the best ductility among these five materials. For central force solids Poisson's ratio is bounded by the lower limit of 0.25 and the upper limit of 0.5. The Poisson's ratio for TiO, TiO_2, Ti_2O_3, Ti_3O, Ti_3O_5 are 0.330, 0.307, 0.287, 0.302 and 0.210, respectively. When ν is between 0.25 and 0.5, it means that the atomic binding force is a central force. Table 2 shows that the atomic binding force of the former materials are central force. TiO possesses the highest ν (0.330), suggesting that it has the weakest stability among the five titanium oxides within the process of resisting shear deformation.

TABLE 2 ELASTIC CONSTANTS C_{IJ}*[GPA]*, SHEAR MODULUS *G[GPA]*, BULK MODULUS *B[GPA]*, YOUNG'S MODULUS *E[GPA],* PUGH MODULUS RATIO *G/B* AND POSSION'S RATIO *N*

name	TiO	TiO_2	Ti_2O_3	Ti_3O	Ti_3O_5
C_{11}	511	278	252	216	305
C_{12}	53	123	97	131	126
C_{13}	53	141	108	79	103
C_{22}	511	252	252	216	213
C_{23}	53	120	107	79	62
C_{33}	511	284	361	304	172
C_{44}	31	94	74	93	55
C_{55}	31	95	74	93	45
C_{66}	31	61	77	43	55
G	78	77	81	67	95
B	205	175	163	146	133
E	209	202	209	173	231
G/B	0.382	0.443	0.498	0.457	0.718
v	0.330	0.307	0.287	0.302	0.210
A^U	6.6849	0.1708	0.1606	1.5695	0.3543

From the all figures A^U unequal to zero, one knows that all five titanium dioxides are anisotropic and TiO is the most anisotropic. But one cannot know the details of the anisotropy. In order to see clearly the elastic anisotropies for TiO, TiO_2, Ti_2O_3, Ti_3O and Ti_3O_5, we plot three dimensional surfaces of modulus in Figure 2. The formulas are as follow [12]:

$$\begin{aligned} E^{-1} = {} & l_1^4 S_{11} + 2l_1^2 l_2^2 S_{12} + 2l_1^2 l_3^2 S_{13} + 2l_1^3 l_3 S_{15} + 2l_2^4 S_{22} + 2l_2^2 l_3^2 S_{23} \\ & + 2l_1 l_2^2 l_3 S_{25} + l_3^4 S_{33} + 2l_1 l_3^3 S_{35} + l_2^2 l_3^2 S_{44} + 2l_1 l_2^2 l_3 S_{45} \\ & + l_1^2 l_3^2 S_{55} + l_1^2 l_2^2 S_{66} \end{aligned} \tag{8}$$

In above formulas, S_{ij} stand for elastic compliance constants, and l_1, l_2 and l_3 are the directional cosine.

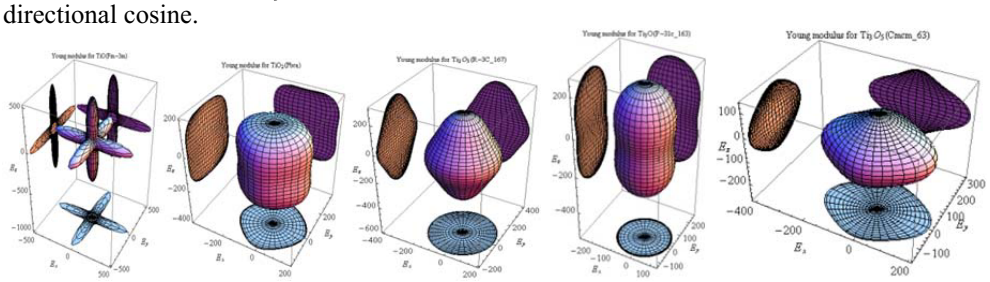


Figure 2. The directional dependence of Young's modulus for TiO, TiO_2, Ti_2O_3, Ti_3O and Ti_3O_5 .

4 Conclusions

In this paper, we calculated the elasticity and anisotropy of Ti_xO_y. The calculated results show that all the five materials are elastically anisotropic. The Anisotropic index A^U, shows the sequences of Ti_xO_y is Ti_2O_3<TiO_2<Ti_3O_5<Ti_3O<TiO. TiO, TiO_2, Ti_2O_3 and Ti_3O show ductility, while Ti_3O_5 shows brittleness.

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