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## The macroscopic elastic anisotropy in tough ceramics from the single crystal elastic behaviour.

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### Abstract

The modern techniques for engineering analysis are based on a deep understanding of the proportional relationship between stress and strain and the description in terms of isotropic elastic constants, in many cases, is enough. In anisotropic materials the knowledge of the elastic constants is important for the manufacturing process and for micro mechanical modelling behaviour of the material to develop the new composite materials.

Theoretical calculations of elastic constants and anisotropies are applied to tough ceramics  $ZrO_2$ ,  $HfO_2$  and in rutile  $TiO_2$  and  $SnO_2$ . Their dependence of the residual hydrostatic stress in the crystal are given. The microscopic elastic anisotropy determined in this work, could be applied in the macro scale in the case the constituent grains have a preferred orientation in the crystal lattice or the grains shape is not spherical (faceted) and it is aligned to a common crystal axis. To cover the case where the grains are distributed at randomly, the Voigt-Reuss-Hill polycrystalline approach is applied to obtain the average values of Young, bulk, shear modules, Poisson coefficient and sound velocity in the transversal and longitudinal modes.

These theoretical results, could be useful in the interpretation of experimental results obtained with the method known as diffraction elastic constant (DEC).

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Elastic properties; anisotropy; ceramics; residual stress

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### 1. Introduction

Oxides of group IV show a common group of properties as high refraction index and high hardness and are used as functional optical coating. Also, their high dielectric constants make them potential material for the development of dielectric gates of sub-micrometer CMOS transistors. The response of

the crystal to external forces characterized by bulk modulus  $B$ , shear modulus  $G$ , Young modulus  $E$  and Poisson coefficients can be determined from the elastic constants  $C_{ij}$ . The ductile-brittle properties of materials are closely related to the response to shear along slide planes, and it is affected by the changes from contributions to the total energy caused by these deformations. The shear elastic constants  $C_{44}$ ,  $C_{55}$  and  $C_{66}$  provide information regarding the bonding properties between adjacent planes of atoms and the anisotropic character of bonds. They are, therefore, useful in determining the structural stability of the crystal. Accurate experimental determinations of elastic constants need large pure single crystals which, in the case of many ceramics, are difficult to obtain. Thus *ab initio* theoretical studies which provide elastic properties of single and poly crystals are appropriate [1,2]. A very important application is the knowledge of biaxial stresses caused by the epitaxial growth of thin films on a given substrate, as in the case of deposition of oxides, different to  $\text{SiO}_2$ , on silicon [100] wafers, used in the electronics industry.  $\text{HfO}_2$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  exhibit tensile stress into the thin-film layers. At room temperature and at pressures above 30 GPa, zirconia, hafnia are transformed into an orthorhombic structure of cotunite type (spatial group  $Pnma$ ) retained in normal condition under decompression but for  $\text{TiO}_2$  is necessary low temperature [3].

$\text{TiO}_2$  and  $\text{SnO}_2$  are crystallized in the rutile structure in normal conditions.  $\text{TiO}_2$  is one of the more important available semiconductors and is widely interesting because of its catalytic, photo-catalytic, and electrochemical properties.  $\text{SnO}_2$  is widely used in chemical sensors (electronic nose). Both oxides have a tetragonal unit cell and the importance of the mechanical properties is in order to quantify the stability of thin and thick films grown on diverse substrates. It is well known that lattice mismatch during film growth give rise to residual stresses which compromise the film stability. Diffraction based methods determine residual stress measuring the strain of the sample [4]. In order to obtain the stress state, the methods require the knowledge of the elastic constants and anisotropies. In the experimental work the elastic deformation is analyzed in different crystalline directions ( $hkl$ ) in a least square loop where the single crystal elastic constants are the refinable parameters. Theoretical *ab-initio* methods predict reliable elastic constant values and relative anisotropies for a single crystal and anisotropies dependence with the structure, composition and material stress state. The complete description of the thermo-elastic properties in a polycrystalline aggregate state can be reached using Voigt, Reuss and Hill (VRH) approaches [5, 6, 7].

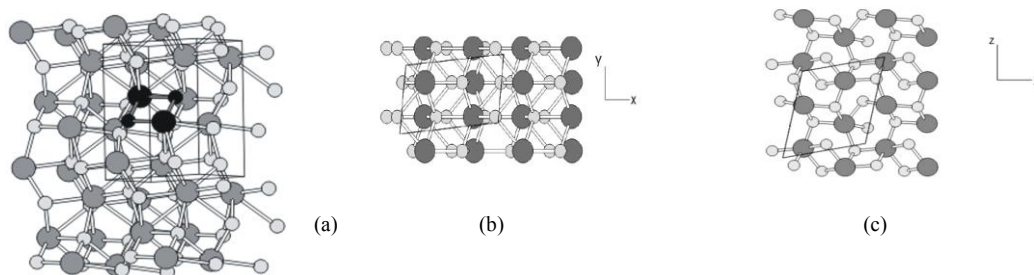
## 2. Methods

The combination of structural databases with computational first principles calculations can predict, easily, the essential elastic properties like  $B$ ,  $E$ ,  $G$  with unprecedented realism. The DFT within LDA and GGA approaches allows the generation of consistent data to existing material, but also the proper prediction of the stability and properties of materials before synthesis, leading to a powerful design capabilities [1, 2, 8, 9](these calculations were validated on a wide range of known materials). With the same computational methods, one can get specific data about well-defined crystals and can investigate systematically the role of defects and impurities in those crystals. SIESTA method [12] represents the valence electrons by a strictly localized basis functions which vanish beyond a certain radius. To deal with the electronic many body effects, SIESTA uses the density functional theory (DFT), in the local density approximation (LDA) and pseudopotentials version to represent the interaction between electrons and ions. The method requires as input the crystal structure, the position and nature of the atoms. Self-consistently calculated, the stability of the system in any phase, is assured by minimizing internal forces on the atoms, which allows to find the equilibrium volume and lattice parameters. The stress tensor can also be calculated by setting constrained restrictions to the lattice, according to Voigt deformations, at normal pressure or at a given target pressure. To minimize internal forces, we apply conjugate gradients to treat the internal atomic optimization.

### 3. Results

#### 3.1 Single crystal and poly crystal at normal pressure

To obtain the elastic constants we follow the methodology described in [10]. Strains were chosen consistent with the symmetry of the system [14].



**Fig. 1.** a) Pnma high density cotunnite structure present in  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ; (b) and (c) some of the applied shear deformations that preserve the symmetry of crystal.

In the case of crystals with rutile symmetry, six different types of strain around the equilibrium position were applied, with a total of 8-10 amplitudes upon each strain. The stress-strain ratios of such set of chosen strains were fitted to Hooke's Law. In the case of cotunnite phase Fig. 1a (orthorhombic with group symmetry  $Pnma$ ), 9 different types of strains were applied (see Fig. 1b,c), with 8-10 amplitudes upon each strain. Since all the amplitudes may exceed the linear elastic limit, fits thereon were necessary done with a 3th degree polynomial; where, the linear part was considered to be the elastic constant  $C_{ij}$ . The aim of this work is to analyze the single crystal elastic constant and anisotropy of young modulus and their dependence with the chemical compositions and residual stress. The crystalline orientation dependence of Young's modulus is shown in selected crystallographic directions for cases herein studied. To get the estimation of the anisotropy from the figures it has to be done the ratio between the higher value of Young's modulus and the lowest one; any value different to the unit shows anisotropic behaviour. The mean values of shear moduli and Poisson's coefficient is obtained applying the polycrystalline Voigt-Reuss-Hill approximation (VRH) [5,6,7] according to the equations of Refs. [10,15].

#### 3.1.1 Effects of the chemical composition and bonding character

To explore the effect of chemical composition on the elastic constants and anisotropies, (Figs. 2a,2b) we show the calculated elastic constants of rutile phase of  $\text{TiO}_2$  and  $\text{SnO}_2$  in Table 1, and derived properties for the poly-crystal in Table 2. It is found that the effect of the nature of the metal atoms Sn and Ti on the elastic properties is not substantially distinguished between  $\text{SnO}_2$  and  $\text{TiO}_2$ , except if pressure is applied ( $\text{SnO}_2$ : Figs. 3a,3b). The bond character: ionic or covalent on the anisotropy shows in  $\text{TiO}_2$  and  $\text{HfO}_2$  a decreasing value when the bond is more ionic. (see Figs. 4a, 4b)

#### 3.1.2 Effects of residual stress

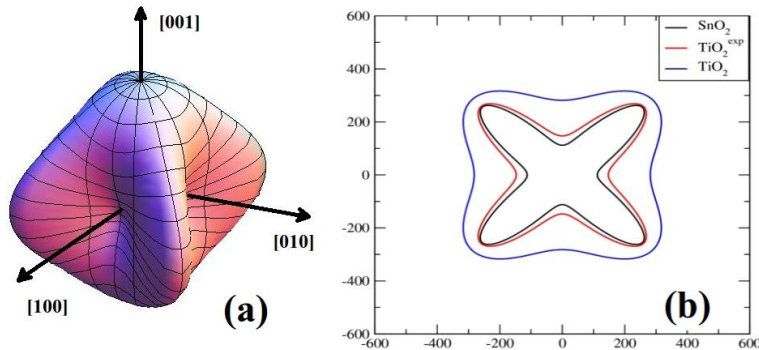
An accurate determination of residual stress in a lattice, using X-Ray diffraction, allows the knowledge of the deformed elastic constants which will move to macro stress. To establish direct relations between the strain and the added stress measured by elastic constants of single crystal, cannot be implemented due to differences in the elastic behaviour of aggregate and the single crystal.

**Table 1** Calculated elastic properties of rutile TiO<sub>2</sub> and SnO<sub>2</sub> at normal pressure. Units are in GPa.

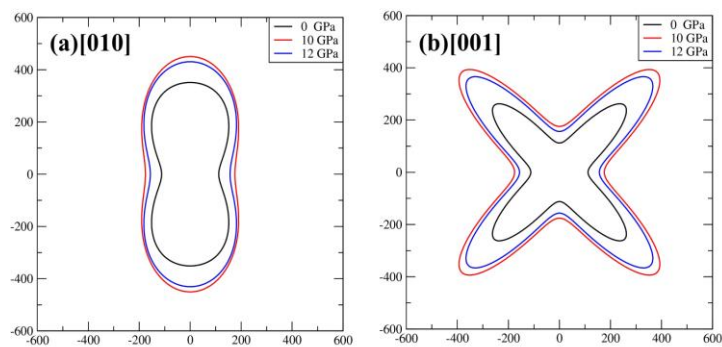
Rutile	C11	C12	C23	C33	C44	C66
TiO <sub>2</sub>	340	143	154	470	141	204
SnO <sub>2</sub>	245	177	155	465	108	209

**Table 2** Thermoelastic properties in the polycrystalline approximation of bulk B, Young E, shear G moduli, averaged sound velocity transverse V<sub>T</sub> and longitudinal V<sub>L</sub>, Poisson coefficient σ and Debye temperature Θ<sub>D</sub> at normal pressure.

Rutile	TiO <sub>2</sub>		SnO <sub>2</sub>		
	0 GPa	SIESTA	Exp. [16]	SIESTA	Exp [17]
B		230	212	207	203
E		373	283	283	218
G		152	113	112	
V <sub>T</sub>		5730	5500	3996	3750
V <sub>L</sub>		9676	10300	7140	6910
σ		0.23	0.28	0.27	
Θ <sub>D</sub>		890	780	576	

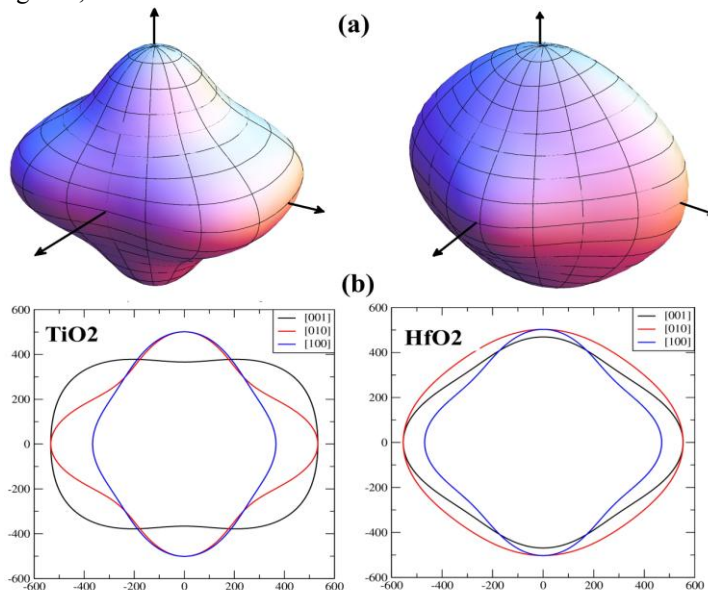


**Fig. 2:** (a) Directional Young modulus surface and (b) projected along the [001] plane of SnO<sub>2</sub> and TiO<sub>2</sub> at 7GPa in rutile structure compared with experimental results ( Isaak DG Carnes J.D Anderson O.L Cyn H, Phys Chem. Minerals, 26, 311998).



**Fig. 3.** (a) Directional Young modulus E(11,12,13) of rutile SnO<sub>2</sub> projected in the XZ plane of SnO<sub>2</sub> (b) The same but in the XY plane, all under pressures of 0, 10 and 12 GPa.

In the aggregate, other effects, such as scattering vector orientation, shape and size of crystalline grain are needed in order to find their elastic properties through diffraction results [4]. The effect of hydrostatic pressures on mechanical properties is analyzed in the case of SnO<sub>2</sub> since it is known that a structural phase transition (of second order) exist between 10 and 12 GPa. Elastic anisotropy in the equilibrium structure in different crystallographic directions is shown in Fig. 3a and 3b; this is the result of allowing the system to fully relax at the transition pressure. It is noted that while the average Young modulus is, generally increased, its anisotropy is maintained in [001] and decreased a 16% in [010]. Rutile TiO<sub>2</sub> under a compression of 8 % of the equilibrium volume (P=7 GPa) shows that the anisotropy is reduced in the [001] direction. Anisotropy changes under pressure in orthorhombic TiO<sub>2</sub> are also shown in Figs. 5a, 5b.



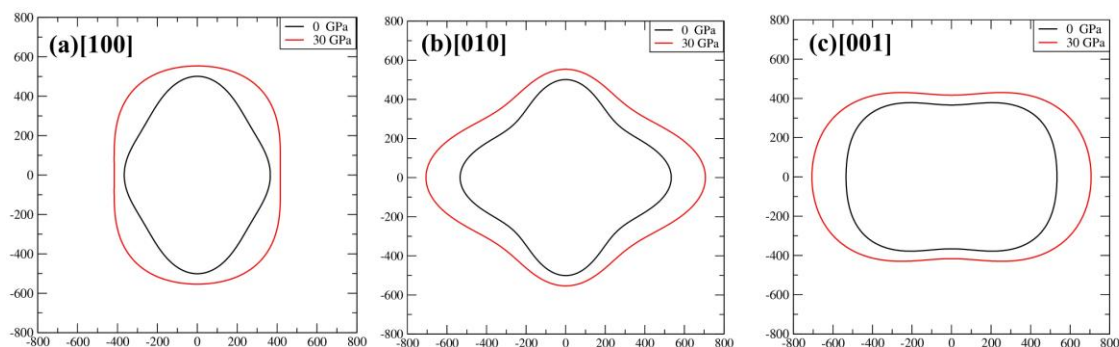
**Fig. 4.** (a) Directional Young Modulus E(11,12,13) for TiO<sub>2</sub> and HfO<sub>2</sub> in the cotunnite structure; (b) Projected E(11,12,13) on planes perpendicular to the crystallographic directions [100], [010] and [001]

**Table 3.** Calculated thermoelastic constants of orthorhombic TiO<sub>2</sub>, ZrO<sub>2</sub> and HfO<sub>2</sub>. B,E,G are in units of GPa, V<sub>i</sub> m/s.

Orthorhombic	TiO <sub>2</sub>	ZrO <sub>2</sub>	HfO <sub>2</sub>
<b>B</b>	370	320	354
<b>E</b>	424	411	453
<b>G</b>	162	160	176
<b>V<sub>T</sub></b>	5436	4985	3210
<b>V<sub>r</sub></b>	10327	9016	7339
<b>σ</b>	0.31	0.27	0.29

**Table 4.** Elastic properties of orthorhombic TiO<sub>2</sub> under the effects of hydrostatic pressure. All units are in GPa.

TiO <sub>2</sub>	C <sub>11</sub>	C <sub>22</sub>	C <sub>33</sub>	C <sub>12</sub>	C <sub>23</sub>	C <sub>13</sub>	C <sub>44</sub>	C <sub>55</sub>	C <sub>66</sub>
<b>0 GPa</b>	688	510	649	129	133	204	258	240	253
<b>30 GPa</b>	800	775	833	208	181	269	346	208	479



**Fig. 5:** Effects of pressure on the orthorhombic  $\text{TiO}_2$  directional Young modulus, projected in planes perpendicular to directions [100], [010], [001] from left to right, respectively.

#### 4. Conclusions

In this work was found that the effect of the nature of the metal atoms Sn and Ti on the elastic properties is not substantially distinguished between  $\text{SnO}_2$  and  $\text{TiO}_2$  in rutile phase, except if hydrostatic pressure is applied. In this case the anisotropy of  $\text{SnO}_2$  is maintained in the [001] and is decreased 16% in [010]. In the case of  $\text{TiO}_2$  under an effective compression of 7 GPa, it is found that the anisotropy is reduced in the [100] direction. The character of the bond: ionic or covalent on the mechanical properties and anisotropies in a common orthorhombic phase among  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$ , shows a decreasing anisotropy when the bond is more ionic. The effect of pressure on the elastic anisotropy of crystallites in the stabilized cotunite  $\text{TiO}_2$  at 30 GPa is to decrease the anisotropy in [100] and [010] and to increase 24% in the [001] respect to the uncompressed sample. These modifications conserved the orthorhombic shape of crystal elastic response.

Finally the patterns of the directional Young modulus could contribute to interpret the directional deformation scheme on the crystal, if the hydrostatic residual stress were presented.

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