# Elastic constants and crystal anisotropy of titanium diboride

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In this study, the elastic constants of a titanium diboride ($TiB_2$) single crystal were measured using resonant ultrasound spectroscopy. In contrast to previous work, the current results are consistent with the measured elastic constants of $TiB_2$ polycrystals. In addition, the crystal anisotropy of $TiB_2$ was examined. The current data show that the elastic properties of $TiB_2$ are much more isotropic than previously considered. © *1997 American Institute of Physics.*
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Titanium diboride ($TiB_2$) has several attractive properties due to its unique electronic structure and bonding nature. It exhibits high elastic moduli, high hardness, and high electric conductivity, which made it a material of considerable interest in many technological applications.

Titanium diboride possesses the hexagonal $AlB_2$ structure,[1] and therefore five elastic constants are required to describe its elastic behavior. Despite the widely reported elastic properties on $TiB_2$,[2–5] only one set of single-crystal elastic constants has been reported,[6] possibly due to the difficulty in obtaining large $TiB_2$ crystals. These constants, shown in Table I, were measured by using a pulse-echo method, except for $C_{13}$, which was estimated. As an evaluation of the previous data, the elastic properties of $TiB_2$ polycrystalline aggregates were estimated from the single-crystal constants using the Hashin–Shtrikman bounds[7] and then compared to the measured $TiB_2$ aggregate elastic properties. To make the comparison, fully dense hot-pressed polycrystalline $TiB_2$, which showed no indication of crystallographic texture, was obtained. Its elastic moduli were measured using a mechanical resonance method.[8] The experimental values and other literature values were listed in Table II. As shown in Table II, the calculated aggregate properties show a large discrepancy from the measured polycrystalline value, which could suggest some errors in the single-crystal elastic constants. In fact, Leiber[9] has also pointed out that these elastic constants should be revised.

The objective of this study was to measure a new set of $TiB_2$ single-crystal elastic constants. The difficulty in obtaining large $TiB_2$ crystals was overcome by using resonant ultrasound spectroscopy which only requires small crystals.[10–12]

A cube of $TiB_2$ single crystal, approximately 2 mm on each side, was used for the measurement. The single crystal was grown using a floating zone technique, which has been detailed elsewhere.[13,14] No major impurities were detected in the single crystal using fluorescent x-ray analysis.[13] However, the boron–titanium phase diagram[15] shows a solid solution range near $TiB_2$, namely, 65.5–67 at. % boron, or $TiB_{1.90}$ to $TiB_{2.03}$. The stoichiometry of the single crystal was determined to be $TiB_{1.97}$.[14]

The $TiB_2$ crystal was oriented using the Laue method[16] and then polished into the shape of a parallelepiped. It is held very lightly at two of its opposing corners between two piezoelectric film transducers (Fig. 1)—one is used as a drive transducer and the other as a receiver. As the drive frequency is swept, the output of the receiver shows peaks at the sample's natural resonances, and these can be compared to theoretical calculations of the normal modes of vibration of an elastic parallelepiped. Using elastic moduli as free parameters, a nonlinear least-squares fit to the resonant frequency data provides accurate estimates of the elastic moduli. In the present work, the published values for $C_{11}, C_{44}$, and $C_{66}$ are used along with the present estimates for $C_{12}$ and $C_{13}$. The latter two are less crucial, as their effect on the frequencies of most modes is smaller than that of the other three moduli. The precision of the determination of elastic constants is usually quite high, a few parts per million. However, the accuracy is limited by the measurements of sample size, and is usually a few percent. The relative sizes of the various elastic constants is usually a few tenth of a percent.

The measured $TiB_2$ single-crystal elastic constants, as well as those reported by Gilman and Roberts[6] are listed in Table I. The $C_{12}$ and $C_{13}$ values were substantially smaller than the prior literature values. Using these new elastic constants, the calculated aggregate elastic properties are in excellent agreement with the measured aggregate values (Table II). This, to some extent, supports the validity of the new constants.

The crystal anisotropy of $TiB_2$ can be qualitatively demonstrated by plotting its Young's modulus as a function of crystallographic direction. The Young's modulus ($E$) of a crystal in a particular crystallographic direction can be calculated by using the following equation:

TABLE I. Single-crystal elastic constants of titanium diboride (GPa).

| | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ |
|---|---|---|---|---|---|
| Gilman and Roberts (Ref. 6) | 690 | 410 | 320 | 440 | 250 |
| This study | 660 | 48 | 93 | 432 | 260 |

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TABLE II. Measured TiB$_2$ polycrystalline elastic moduli and theoretical values derived from single-crystal elastic constants by using the Hashin–Shtrikman bounds.

| | Young's modulus (GPa) | Shear modulus (GPa) |
|---|---|---|
| Theoretical values: Gilman and Roberts (Ref. 6) | | |
| Upper bound | 451 | 171 |
| Lower bound | 445 | 168 |
| Theoretical values: This study | | |
| Upper bound | 580 | 263 |
| Lower bound | 578 | 262 |
| Measured values[a]: This study | 569 | 259 |
| Literature values[a]: Reference 5 | 568 | 258 |

[a]The values have been adjusted for the effect of porosity. In this study, Gibson and Ashby equation (Ref. 17) was employed for the correction. The equation can be written as $E = E_0(1 - 2P + P^2)$, where $E$ and $P$ are the measured modulus and porosity, respectively, and $E_0$ is the modulus of the fully dense material.

$$\frac{1}{E} = s_{11}(1 - a_3^2)^2 + s_{33}a_3^4 + (2s_{13} + s_{44})(a_3^2 - a_3^4), \quad (1)$$

where $s_{ij}$ is compliance and $a_3$ is the direction cosine between the direction and the $c$ axis. The results are shown in Fig. 2. It is apparent that the new elastic constants indicate that TiB$_2$ is more isotropic and stiffer than previously considered.

The degree of crystal anisotropy of materials can be quantified in various ways, depending on crystal structure. For hexagonal crystals, two parameters are needed to describe crystal anisotropy: anisotropies of compressibility ($A_{comp}$) and shear ($A_{shear}$). They can be written as[18]

$$A_{comp} = \frac{s_{33} + 2s_{13}}{s_{11} + s_{12} + s_{13}} \quad (2)$$

and

$$A_{shear} = \frac{2c_{44}}{c_{11} - c_{12}}, \quad (3)$$

where $c_{ij}$ and $s_{ij}$ are the elastic stiffness and compliance, respectively. $A_{shear}$ is the Zener ratio, i.e., the ratio of shear moduli in {100} planes and {110} planes in the ⟨100⟩ direc-
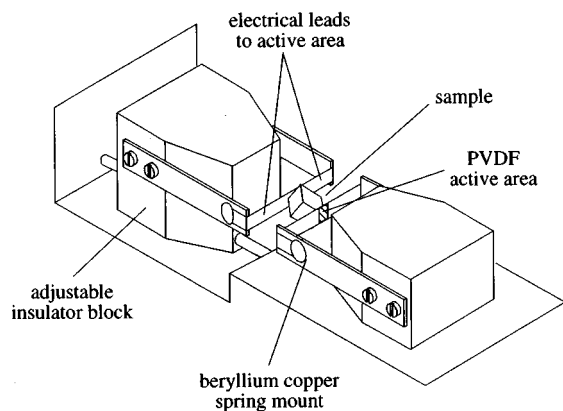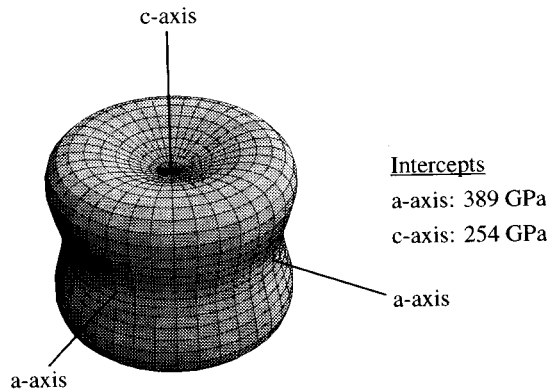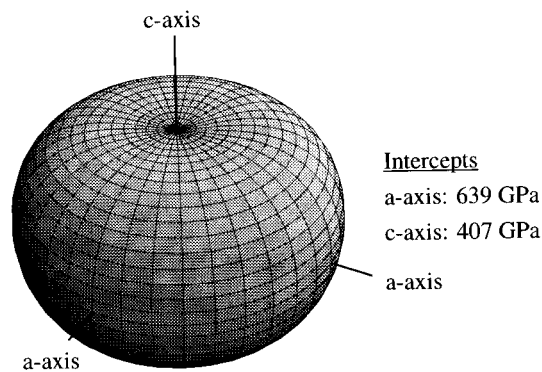
FIG. 1. Resonant ultrasound spectroscopy apparatus for the measurement of single-crystal elastic constants.

(a)

(b)

FIG. 2. Three-dimensional surfaces representing the Young's modulus of titanium diboride in different crystallographic directions according to the elastic constants measured by (a) Gilman and Roberts (Ref. 6) and (b) this study.

tions. The two anisotropy indices were calculated and are listed in Table III. Note that for these two parameters, a value of one indicates elastic isotropy. As the possible values range from zero to infinity, however, these parameters can be ambiguous. Alternatively, the "percentage anisotropies" in compressibility and shear can be defined by[18]

$$A_{comp}^* = \frac{K_V - K_R}{K_V + K_R} \quad (4)$$

TABLE III. Elastic anisotropy of TiB$_2$.

| | | | Percentage anisotropy | |
|---|---|---|---|---|
| | $A_{comp}$ | $A_{shear}$ | $A_{comp}^*$(%) | $A_{shear}^*$(%) |
| Gilman and Roberts (Ref. 6) | 3.83 | 1.79 | 4.40 | 6.32 |
| This study | 1.54 | 0.85 | 1.27 | 1.54 |

and

$$A^*_{shear} = \frac{G_V - G_R}{G_V + G_R},\qquad(5)$$

where $K$ and $G$ are the bulk and shear moduli, and the subscripts $V$ and $R$ represent the Voigt and Reuss bounds[19,20] for the polycrystalline aggregate elastic properties. For these two expressions, a value of zero represents elastic isotropy and a value of one (100%) is the largest possible anisotropy. The ''percentage anisotropies'' of $TiB_2$ were listed in Table III. Clearly, the new elastic constants exhibit less elastic anisotropy than previously reported single-crystal values.

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