Research Article

Vibrational Spectroscopy of Binary Titanium Borides: First-Principles and Experimental Studies

Urszula D. Wdowik,¹ Agnieszka Twardowska,¹ and Bogusław Rajchel²

¹*Institute of Technology, Pedagogical University, Podchorążych 2, 30-084 Krakow, Poland*

²*Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Krakow, Poland*

Correspondence should be addressed to Urszula D. Wdowik; sfdowik@cyf-kr.edu.pl

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Vibrational dynamics of binary titanium borides is studied from first-principles. Polarized and unpolarized Raman spectra of TiB, TiB₂, and Ti₃B₄ are reported along with the experimental spectra of commercial powder and bulk TiB₂ containing less than 1 wt.% of impurity phases. The X-ray diffraction spectroscopy, applied for phase composition examination of both bulk and powder materials, identifies only the TiB₂ phase. The simulated Raman spectra together with literature data support interpretation and refinement of experimental spectra which reveal components arising from titanium dioxide (TiO₂) and amorphous boron carbide (B₄C) impurity phases as well as graphitic carbon. These contaminations are the by-products of synthesis, consolidation, and sintering aids employed to fabricate powder and bulk titanium diboride.

1. Introduction

Generally, the Ti–B system comprises three compounds, namely, TiB, TiB₂, and Ti₃B₄ [1]. These borides have attracted much experimental and theoretical research because of their unique properties such as high melting point, high hardness, high elastic modulus, good thermal and electrical conductivity, excellent oxidation resistance, and considerable chemical stability [2]. The combination of these properties makes titanium borides promising materials for multifunctional applications, for example, electrode materials, cutting tools, wear-resistant parts, protecting coatings, and all kinds of high-temperature structural components [3].

The most extensively studied TiB₂ compound has recently gained renewed experimental interest due to its application for deposition of thin Ti–B films [4–6]. We note that chemical composition of Ti–B film varies with applied conditions of deposition, and hence the phase composition of deposited material differs from that desired and expected. An analysis of the phase composition of thin and frequently amorphous (or partially amorphous) Ti–B films by the X-ray diffraction (XRD) method remains uncertain due to the content of light boron element. Therefore, for characterization of deposited

thin Ti–B films, some complementary methods, such as the Raman spectroscopy, have to be applied. On the other hand, reference Raman spectra are usually based on measurements carried out on samples prepared in different conditions, and thus the resulting Raman spectra show differences in position, intensities, and even the number of peaks among the spectra recorded for the same phase and analyzed in very similar experimental conditions. In order to resolve these ambiguities one may calculate positions and intensities of the Raman-active modes for a given system using the currently available theoretical tools such as those based on state-of-the-art density functional theory (DFT). Results of numerical simulations can then be used for interpretation and refinement of respective experimental spectra.

So far, a number of theoretical and experimental works have been done to investigate the structural, electronic, and elastic properties of titanium borides [7–11], leaving their dynamical properties highly unexplored [12, 13]. This research extends and supplements the present knowledge on titanium borides by providing information on their vibrational properties. In particular, the positions and intensities of the Raman-active phonons of TiB, TiB₂, and Ti₃B₄ are determined from first-principles calculations by using the DFT

theory and the direct method. We also provide interpretation of the Raman spectra measured for commercially available powder and bulk samples of titanium diboride. Results of these studies are hoped to stimulate further experimental and theoretical progress in the field of Ti–B system.

2. Methodology

2.1. Experimental. Experiments were performed for commercial TiB_2 powder (H. C. Starck, Germany) and bulk (target, Goodfellow, UK) samples. The grain size of TiB_2 powder with purity of about 99 wt.% was in the range 2.5–3.5 μm . The target sample of 30 mm in diameter and 4 mm in thickness was mechanically polished on one side using diamond grinding (9, 6, and 3 μm) and finally polished in 1 μm suspension. At each polishing step, the surface was degreased by 2-Propanol and then ultrasonically cleaned in acetone bath for 5 minutes. After drying (in air), the target was mounted in a vacuum chamber to perform ion cleaning at room temperature and pressure of 10^{-2} Pa. The iron cleaning was done by a beam of Ar^+ ions of energy of 10 keV directed at sample at an angle of 65° (measured to the normal of target surface). Such preparation procedure is required for the Raman measurements as the spectrometer used in our studies is equipped with the confocal (light) microscope. Moreover, the target is further used for deposition of TiB_2 thin films by the PVD method (results not discussed in the present paper).

Phase identification was performed by the X-ray diffraction (XRD) method using PANalytical Empyrean diffractometer. The CuK_α radiation (intended $\lambda = 1.5406 \text{ \AA}$, intensity ratio $\text{CuK}_{\alpha_1}/\text{CuK}_{\alpha_2} = 2$, $U = 40 \text{ kV}$, $I = 30 \text{ mA}$) in the Bragg-Brentano configuration was used for this purpose. The XRD patterns were collected in 2θ geometry over the scattering angles ranging from 20° to 82° with a step size of 0.02° . Analysis was performed according to the ICSD database and the Rietveld method which took into account the ratio $\text{CuK}_{\alpha_1}/\text{CuK}_{\alpha_2} = 2$.

The Raman spectroscopy was applied to refine the phase composition of both powder and bulk (target) samples. To excite Raman spectra, the Nd:YAG laser beam with wavelength of 532 nm and a power of 6.25 mW was used. Unpolarized Raman spectra in backscattering geometry were collected at room temperature using the Thermo-Nicolet Raman ALMEGA XR dispersive confocal spectrometer operating in the micro-Raman mode. Raman spectra were recorded with normal (4 cm^{-1}) and high-spectral (2 cm^{-1}) resolutions.

2.2. Theoretical. Calculations were carried out within the DFT method implemented in the VASP code [14, 15]. Electron-ion interaction was represented by the projector augmented wave (PAW) method. The generalized gradient approximation with parametrization of Perdew, Burke, and Ernzerhof (GGA-PBE) [16, 17] was applied for the exchange and correlation potential. The wavefunctions were expanded in a plane-wave basis set with a cutoff energy of 420 eV. Reference configurations for valence electrons were ($3d^3 4s^1$) for Ti and ($2s^2 2p^1$) for B. Lattice constants and internal atomic positions of TiB , TiB_2 , and Ti_3B_4 unit cells were

fully optimized with convergence criteria for the residual Hellman-Feynmann (HF) forces and the system's total energy of $10^{-5} \text{ eV \AA}^{-1}$ and 10^{-7} eV , respectively. The Brillouin zones of TiB , TiB_2 , and Ti_3B_4 were sampled using, respectively, 54, 96, and 50 irreducible $\mathbf{k}$ -points generated according to the Monkhorst-Pack scheme. Phonon calculations were performed within the direct method approach [18, 19] and harmonic approximation. The HF forces were obtained by displacing the symmetry nonequivalent Ti and B atoms from their equilibrium positions by $\pm 0.02 \text{ \AA}$ in the supercells containing 64 atoms (TiB), 92 atoms (TiB_2), and 112 atoms (Ti_3B_4). The HF forces were calculated with reduced number of $\mathbf{k}$ -points. The total number of calculated displacements amounted to 12 for TiB , 6 for TiB_2 , and 24 for Ti_3B_4 . Peak intensities of the nonresonant Raman spectrum (in Stokes process) were calculated from the well-known expression [20]: $I \propto |\mathbf{e}_s \mathbf{R} \mathbf{e}_i|^2 \omega^{-1} (n+1)$, where $(n+1)$ is the population factor for Stokes scattering with $n = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ denoting the Bose-Einstein thermal factor, $\mathbf{e}_i$ ($\mathbf{e}_s$) is the polarization of the incident (scattered) radiation, and $\mathbf{R}$ is the Raman susceptibility tensor. The components of $\mathbf{R}$ tensor (α_{ij}) were determined from derivatives of the electric polarizability tensor over the atomic displacements [19, 21, 22]. The electric polarizabilities were calculated within the linear-response method [23] and for each symmetry nonequivalent atom was displaced from its equilibrium position by $\pm 0.01 \text{ \AA}$. Details of calculations can also be found elsewhere [24, 25]. We also note that anharmonic effects leading to changes in phonon frequencies and reflected by shifts of the Raman peaks' positions have been neglected. This is mainly because our measurements are performed at room temperature, where the effects related to the thermal expansion of compounds from the Ti–B system are negligible. Also, the effect of anharmonicity on the widths of Raman peaks is not considered in the present work. Thus, the Raman peaks are simulated by Lorentzian functions with artificial FWHMs corresponding to energy resolution of the Raman spectrometer used in our studies.

3. Results and Discussion

3.1. Structural Properties. Titanium monoboride (TiB) crystallizes in the orthorhombic FeB structure with the space group $Pnma$ (no. 62) [26], where both Ti and B atoms occupy (4c) lattice sites. Its primitive unit cell consists of 8 atoms (4 formula units). The main building block of TiB is the trigonal prism with the B atom at the center and the Ti atoms in corners. The transverse stacking of the trigonal prisms in columnar arrays leads to a zig-zag chain of B atoms along the $[010]$ direction, as schematically shown in Figure 1.

Titanium diboride (TiB_2) has hexagonal, layered structure of AlB_2 -type (space group $P6/mmm$, no. 191) with Ti and B atoms located, respectively, at (1a) and (2d) Wyckoff positions [27]. The primitive unit cell of TiB_2 consists of 3 atoms (1 formula unit). The TiB_2 crystal structure is presented in Figure 2. Each Ti atom is surrounded by 12 equidistant B atoms, whereas each B atom has 3 B atoms at a short distance and 6 Ti atoms at a much longer distance. The B-sublattice

FIGURE 1: The $2 \times 2 \times 1$ supercells of TiB. Blue and green balls denote Ti and B atoms, respectively. Dashed box represents the unit cell of TiB crystal.

FIGURE 2: The $2 \times 2 \times 2$ supercell of TiB_2 . Blue and green balls denote Ti and B atoms, respectively. Dashed box represents the unit cell of TiB_2 crystal.

resembles that of graphitic carbon. The Ti-sublattice is nested in the interstices provided by the B-sublattice.

Typical X-ray diffraction spectra of commercial powder and bulk samples of TiB_2 are shown in Figure 3. The XRD patterns of powder and target TiB_2 are very similar to each other and the Rietveld analysis confirms that the samples contain titanium diboride as a majority phase with the lattice constants $a_{\text{powder}} = 3.0178 \text{ \AA}$, $c_{\text{powder}} = 3.2160 \text{ \AA}$, $a_{\text{target}} = 3.0324 \text{ \AA}$, and $c_{\text{target}} = 3.2345 \text{ \AA}$ which correspond to other experimental studies [27] ($a = 3.0292 \text{ \AA}$ and $c = 3.2284 \text{ \AA}$).

The crystal structure of Ti_3B_4 is orthorhombic (space group $Immm$, no. 71) and isomorphous with that of Ta_3B_4 [28]. There are 2 nonequivalent B atoms at $(4i)$ and $(4j)$ lattice sites. Also Ti atoms reside in 2 different Wyckoff positions, namely, $(2d)$ and $(4i)$. Thus, the primitive unit cell of Ti_3B_4 contains 14 atoms. The crystal structure of Ti_3B_4 is displayed in Figure 4.

Parameters of the TiB, TiB_2 , and Ti_3B_4 structures determined at the ground state are summarized in Table 1, along with the available experimental data for comparison. In general, the calculated structural parameters of the Ti-B compounds remain in very good agreement with results of the previous experiments [26–28]. Therefore, our theoretical bond lengths between boron atoms (B–B), titanium and boron atoms (Ti–B), and between titanium atoms (Ti–Ti), which are collected in Table 2, closely correspond to those observed in experimental studies. In all considered titanium borides, the shortest bond lengths ($\sim 1.8 \text{ \AA}$) are found between B atoms. The Ti–B bonds are much longer ($\sim 2.4 \text{ \AA}$) as

compared to B–B bonds, but shorter than the Ti–Ti bonds ($\sim 2.9 \text{ \AA}$). The values of interatomic distances reflect the nature of bonding in titanium borides. This has already been discussed in numerous theoretical studies considering the electronic structure of these compounds [7–11]. Results of the present research confirm that the chemical bonding in TiB, TiB_2 , and Ti_3B_4 is a mixture between covalent, ionic, and metallic bonding. Strong covalent bonds exist between B atoms, while mixed metallic-covalent bonds are between Ti atoms. There is also a mixed ionic-covalent interaction between Ti and B atoms.

3.2. Zone-Center Phonon Modes. The optically active zone-center phonon modes in TiB, TiB_2 , and Ti_3B_4 are either Raman-active (*gerade*) or infrared- (IR-) active (*ungerade*) due to the presence of inversion symmetry in these systems. The Γ -point phonon modes in TiB can be decomposed into the irreducible representations of the point group D_{2h}^{16} as follows: $4A_g \oplus 2A_u \oplus 2B_{1g} \oplus 4B_{1u} \oplus 4B_{2g} \oplus 2B_{2u} \oplus 2B_{3g} \oplus 4B_{3u}$. Among them 3 modes ($B_{1u} \oplus B_{2u} \oplus B_{3u}$) are lattice translational modes and A_u ones are silent (optically inactive). The modes with symmetries A_g , B_{1g} , B_{2g} , and B_{3g} are Raman-active, whereas modes B_{1u} , B_{2u} , and B_{3u} are IR-active. Both Ti and B atoms occupying the $(4c)$ lattice positions contribute to the Raman and IR-active modes. The optical IR modes of B_{1u} and B_{3u} symmetries correspond to the oscillations of the dipole moment within the crystal ac -plane, whereas those of B_{2u} symmetry to the oscillations parallel the crystal b -axis. The A_g and B_{2g} phonons involve vibrations of

FIGURE 3: X-ray diffraction spectra of (a) powder (H. C. Starck, Germany) and (b) bulk (target, Goodfellow, UK) samples of titanium diboride (TiB_2). Experimental data and the Rietveld refinement are represented by symbols and curves, respectively. Small vertical lines indicate positions of the Bragg peaks corresponding to the TiB_2 phase. The XRD peaks are indexed according to the reference 04-010-8469 [27].

FIGURE 4: The $1 \times 2 \times 1$ supercell of Ti_3B_4 . Blue and green balls denote Ti and B atoms, respectively. Dashed box represents the unit cell of Ti_3B_4 crystal.

TABLE 1: Structural parameters of TiB , TiB_2 , and Ti_3B_4 determined at the ground state and from experiments [26–28].

Parameter	Present	Experiment
TiB ($Pnma$, no. 62)		[26]
a (Å)	6.1105	6.12
b (Å)	3.0504	3.06
c (Å)	4.5623	4.56
Ti (4c)	(0.1772, 1/4, 0.1214)	(0.177, 1/4, 0.123)
B (4c)	(0.0298, 1/4, 0.5985)	(0.029, 1/4, 0.603)
TiB_2 ($P6/mmm$, no. 191)		[27]
a (Å)	3.0336	3.0292
c (Å)	3.2261	3.2284
Ti (1a)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)
B (2d)	(1/3, 2/3, 1/2)	(1/3, 2/3, 1/2)
Ti_3B_4 ($Immm$, no. 71)		[28]
a (Å)	3.2596	3.259
b (Å)	13.7374	13.737
c (Å)	3.0389	3.036
Ti_1 (2d)	(1/2, 1/2, 0.0)	(1/2, 1/2, 0.0)
Ti_2 (4i)	(0.0, 0.1858, 0.0)	(0.0, 0.18, 0.0)
B_1 (4i)	(0.0, 0.3684, 0.0)	(0.0, 0.37, 0.0)
B_2 (4j)	(0.0, 0.4356, 1/2)	(0.0, 0.44, 1/2)

the Ti- and B-sublattices within the ac -plane, while the B_{1g} and B_{3g} phonons arise from atomic vibrations along the b -axis. The frequencies of the Raman and IR-active

TABLE 2: Interatomic distances (in Å) for titanium borides.

Compound	B–B	Ti–B	Ti–Ti
TiB	1.81	2.35	2.87
TiB_2	1.75	2.38	3.03
Ti_3B_4	1.77 ($\text{B}_2\text{--B}_2$)	2.33 ($\text{Ti}_2\text{--B}_2$)	2.84 ($\text{Ti}_2\text{--Ti}_2$)
	1.78 ($\text{B}_1\text{--B}_1$)	2.35 ($\text{Ti}_2\text{--B}_1$)	2.97 ($\text{Ti}_1\text{--Ti}_2$)
	3.04 ($\text{B}_1\text{--B}_2$)	2.40 ($\text{Ti}_1\text{--B}_2$)	3.04 ($\text{Ti}_1\text{--Ti}_1$)
		2.43 ($\text{Ti}_1\text{--B}_1$)	

phonon modes predicted by our calculations for TiB are listed in Table 3. The silent A_u modes are found at 280.2 and 453.1 cm^{-1} . The IR modes gather into 2 bands with lower-frequency band located at $\sim 250 \text{ cm}^{-1}$ and the higher-frequency band extending from about 470 to 560 cm^{-1} . Similarly, the Raman modes are also concentrated within 2 bands. The lower-frequency band ranges from about 260 to 350 cm^{-1} and the higher-frequency one from 570 to 780 cm^{-1} .

Phonons at the Brillouin zone center of the TiB_2 structure can be classified according to the irreducible representations of the point group D_{6h}^1 as follows: $A_{2u} \oplus B_{1g} \oplus 2E_{2g}^{(2)} \oplus 2E_{1u}^{(2)}$. The modes with A_{2u} and E_{1u} symmetries are IR-active, the modes of E_{2g} symmetry are Raman-active, and the B_{1g} mode is silent. Modes E_{2g} and E_{1u} remain doubly degenerate. The $A_{2u} \oplus E_{1u}^{(2)}$ phonons constitute lattice translational modes. The IR-active A_{2u} and E_{1u} modes are related to the dipole moment oscillations perpendicular and parallel to the crystal hexagonal plane, respectively. In the Raman-active E_{2g} modes

TABLE 3: Frequencies of the Raman and IR-active phonon modes in TiB. Units: cm^{-1} .

Mode symmetry	Raman	Infrared
B_{1u}		245
B_{3u}		255
A_g	259	
B_{3g}	272	
B_{2g}	293	
B_{1g}	299	
A_g	305	
B_{2g}	347	
B_{3u}		468
B_{1u}		494
B_{2u}		499
B_{3u}		542
B_{1u}		564
A_g	570	
B_{2g}	607	
B_{2g}	634	
A_g	639	
B_{1g}	760	
B_{3g}	780	

the Ti atoms are at rest, and hence these modes are only associated with the B atoms vibrating within the hexagonal plane. The E_{2g} Raman phonon appears at 883.1 cm^{-1} and the infrared E_{1u} and A_{2u} phonons have frequencies of 515.1 cm^{-1} and 521.5 cm^{-1} , respectively. The calculated frequency of the silent B_{1g} amounts to 557.9 cm^{-1} . The frequencies of the Raman and infrared modes in TiB_2 crystal determined in the present DFT studies closely correlated with those obtained previously [12, 13].

The Γ -point phonon modes in Ti_3B_4 can be decomposed into the irreducible representations of the point group D_{2h}^{25} in the following way: $3A_g \oplus 3B_{1g} \oplus 3B_{3g} \oplus 4B_{1u} \oplus 4B_{2u} \oplus 4B_{3u}$, where the Raman modes have symmetries of A_g , B_{2g} , and B_{3g} . The B_{1u} , B_{2u} , and B_{3u} modes are infrared-active. There are 3 acoustic modes constituted by the IR phonons ($\Gamma_{\text{acoustic}} = B_{1u} \oplus B_{2u} \oplus B_{3u}$). The IR-active B_{1u} , B_{2u} , and B_{3u} are associated with the oscillations of the dipole moment along the crystallographic c , b , and a axes, respectively. The Ti₁ atoms residing in $(2d)$ sites do not contribute to the Raman modes. Therefore, the A_g , B_{2g} , and B_{3g} phonons results from the displacements of Ti₂, B₁, and B₂ atoms along the c , a , and b axes of the Ti_3B_4 crystal. Respective frequencies of the Raman and IR modes are collected in Table 4.

3.3. Raman Spectra. The Raman tensors of the A_g , B_{1g} , B_{2g} , and B_{3g} phonon modes in TiB have the following nonzero components:

$$\begin{aligned} A_g: \quad & \alpha_{xx} = a, \\ & \alpha_{yy} = b, \\ & \alpha_{zz} = c, \end{aligned}$$

TABLE 4: Frequencies of the Raman and IR-active phonon modes in Ti_3B_4 . Units: cm^{-1} .

Mode symmetry	Raman	Infrared
B_{3g}	249	
B_{1g}	263	
B_{1u}		277
B_{3u}		287
B_{2u}		313
A_g	323	
B_{2u}		483
B_{1u}		488
B_{3g}	499	
B_{1g}	504	
B_{3u}		528
A_g	550	
B_{3u}		556
B_{1g}	574	
B_{2u}		715
B_{1u}		804
B_{3g}	829	
A_g	835	

$$B_{1g}: \quad \alpha_{xy} = \alpha_{yx} = d,$$

$$B_{2g}: \quad \alpha_{xz} = \alpha_{zx} = e,$$

$$B_{3g}: \quad \alpha_{yz} = \alpha_{zy} = f$$

(1)

and the polarization selection rules [29] for the point group D_{6h}^1 allow the polarized Raman scattering experiments to determine phonons having particular symmetries. In the backscattering geometry, where the wave vector of incident ($\mathbf{k}_i$) and scattered ($\mathbf{k}_s$) radiations remain antiparallel, the modes of A_g symmetry can be measured, for example, at $Z(XX)\bar{Z}$ scattering configuration (in Porto's notation). In order to observe the B_{1g} , B_{2g} , and B_{3g} modes one needs to apply the $Z(XY)\bar{Z}$, $Y(XZ)\bar{Y}$, and $X(YZ)\bar{X}$ scattering geometries, respectively. The polarized backscattering Raman spectra at scattering configurations outlined above are shown in Figure 5. One notes that not all Raman-active modes of TiB are intense enough to be experimentally observed.

The Raman spectrum of TiB_2 single crystal is characterized by a single peak due to the mode of E_{2g} symmetry, which can be detected at $Z(XY)\bar{Z}$ scattering geometry. The corresponding Raman tensor of the doubly degenerate E_{2g} phonon mode has the following form:

$$\begin{aligned} E_{2g}^{(1)}: \quad & \alpha_{xx} = d, \\ & \alpha_{yy} = -d, \end{aligned} \tag{2}$$

$$E_{2g}^{(2)}: \quad \alpha_{xy} = \alpha_{yx} = -d.$$

The Raman tensors of the A_g , B_{1g} , and B_{3g} modes in Ti_3B_4 crystal are defined in the same manner as for the TiB

FIGURE 5: Backscattering Raman spectra of TiB crystal calculated at scattering geometries (a) $Z(XX)\bar{Z}$, (b) $Z(XY)\bar{Z}$, (c) $Y(XZ)\bar{Y}$, and (d) $X(YZ)\bar{X}$. Spectra are simulated at 300 K and with laser excitation wavelength of 532 nm. Peaks are represented by Lorentzian functions with artificial FWHMs of 2 cm^{-1} .

FIGURE 6: Backscattering Raman spectra of Ti_3B_4 crystal calculated at scattering geometries (a) $Z(XX)\bar{Z}$, (b) $Z(XY)\bar{Z}$, and (c) $X(YZ)\bar{X}$. Spectra are simulated at 300 K and with laser excitation wavelength of 532 nm. Peaks are represented by Lorentzian functions with artificial FWHMs of 2 cm^{-1} .

crystal (see (1)). Therefore, one determines the A_g , B_{1g} , and B_{3g} phonons in Ti_3B_4 by using the same scattering geometries as those given for orthorhombic TiB crystal. The resulting Raman spectra are presented in Figure 6.

In majority of cases, experimental characterization of the Ti-B material by using the Raman spectroscopy is based on measurements performed on powder samples, and hence the resulting spectra of polycrystalline materials may differ from those for single crystals. Indeed, the simulated unpolarized Raman spectra in backscattering geometry of TiB, TiB_2 , and Ti_3B_4 polycrystals, which are shown in Figure 7, remain quite distinct from the polarized spectra of the respective single crystals given in Figures 5 and 6. First of all,

not all Raman-active modes are observed due to their weak intensities. The peaks of TiB and Ti_3B_4 polycrystals originate from phonons of the A_g symmetry. Therefore, the unpolarized Raman spectrum of multiphase Ti-B system may consist of three bands. The low-frequency ($240\text{--}360\text{ cm}^{-1}$) and middle-frequency ($520\text{--}680\text{ cm}^{-1}$) bands are expected to be dominated by the modes of TiB and Ti_3B_4 phases, whereas the high-frequency band ($800\text{--}900\text{ cm}^{-1}$) is expected to be dominated by the modes of TiB_2 and Ti_3B_4 phases.

According to the group symmetry analysis, the TiB_2 compound exhibits a single doubly degenerate Raman-active mode of E_{2g} symmetry, which should be revealed by the Raman spectra of either a single crystal or polycrystalline

FIGURE 7: Unpolarized Raman spectra of TiB, TiB₂, and Ti₃B₄ polycrystals calculated at backscattering geometries. Spectra are simulated at 300 K and with laser excitation wavelength of 532 nm. Peaks are represented by Lorentzian functions with artificial FWHMs of 2 cm⁻¹.

FIGURE 8: Experimental Raman spectrum of commercial TiB₂ powder (H. C. Starck, Germany) measured at room temperature with laser excitation wavelength of 532 nm.

samples. However, a typical Raman spectrum of TiB₂ commercial powder sample shows more rich experimental pattern than that predicted theoretically. Such spectrum is presented in Figure 8. It shows a small intensity peak at 143 cm⁻¹ and broad high-intensity peaks at 260, 420, and 610 cm⁻¹. These peaks are characteristic for rutile titanium dioxide (TiO₂) phase, whose vibrational spectrum has 4 vibrational bands centered around 145 cm⁻¹ (B_{1g}), 445 cm⁻¹ (E_g), 610 cm⁻¹ (A_{1g}), and 240 cm⁻¹ for second-order scattering effect (SOE) [30, 31]. We note that similar spectrum was also obtained for commercial powder TiB₂, although with slightly different positions of the Raman peaks (260, 409, and 598 cm⁻¹), and it was assigned to the anatase phase of TiO₂ [32]. Our spectrum is unlikely to represent powder anatase TiO₂, as such spectrum usually shows 5 Raman modes centered around 144 cm⁻¹ (E_g),

FIGURE 9: Experimental Raman spectrum of commercial TiB₂ target (Goodfellow, UK) measured at room temperature with laser excitation wavelength of 532 nm.

196 cm⁻¹ (E_g), 394 cm⁻¹ (B_{1g}), 516 cm⁻¹ ($B_{1g} + A_{1g}$), and 638 cm⁻¹ (E_g) [30, 33, 34]. Moreover, the characteristic feature of anatase spectrum is the high-intensity peak at 144 cm⁻¹ which dominates over the remaining peaks having comparably smaller intensities. In addition, the high-frequency range of our spectrum reveals two quite intense peaks at about 1360 and 1570 cm⁻¹ indicating the presence of graphitic carbon with sp^2 and sp^3 bonds [35]. Nevertheless, we confirm that even a small amount of contaminating phase, such as TiO₂ and unreacted carbon, being by-products of the carbothermal reduction process employed to fabricate TiB₂ powder according to the following reaction [36]:

can prevail in the Raman spectrum of commercial TiB₂ powder.

TiB₂ can also be prepared by reduction of TiO₂ by boron carbide (B₄C) and carbon as follows [37]:

The above procedure is frequently applied to produce commercial targets of TiB₂. Thus, the Raman spectrum of such target usually shows a dominant contribution from the by-products of synthesis and consolidation reactions, as shown in Figure 9. Here, the main peaks appearing at 271, 318, 480, 532, 728, 827, 1000, and 1089 cm⁻¹ are associated with the amorphous B₄C phase which displays characteristic Raman bands at 270, 320, 481, 531, 728, 830, 1000, and 1088 cm⁻¹ [38–40]. Additionally one detects a weak feature at about 970 cm⁻¹ which is also visible in the previously measured spectra of crystalline and amorphous boron carbide [39, 40]. Besides, our Raman spectrum of target sample reveals a peak at 881 cm⁻¹ being an evidence of the presence of TiB₂ phase, for which a Raman peak was predicted by our DFT calculations at 883 cm⁻¹.

4. Summary and Conclusions

The present work reports on experimental Raman spectra of commercially available powder and bulk samples of titanium diboride. It is shown that micro-Raman spectroscopy enables identification of impurity phases contained in the samples even though their concentration remains below 1 wt.%. Detailed analysis uncover contamination of commercial TiB_2 powder and bulk samples by TiO_2 and B_4C phases, respectively, which are the by-products of chemical reactions applied to produce samples. Additionally, the graphitic carbon is identified as a *fingerprint* of sintering aids used in production process of bulk TiB_2 . Vibrational properties of titanium borides (TiB , TiB_2 , and Ti_3B_4), in particular, positions and intensities of the Raman-active phonons, were gained from theoretical approach based on the DFT method. Theoretical Raman spectra were simulated at conditions close to those encountered in experiments and for ideal crystals, namely, free of defects and residual stresses which are always present in real samples due to their preparation procedure. Thus, our *ab initio* results can serve not only as a guide for interpretation of experimental Raman spectra or symmetry mode assignment in particular titanium borides, but also for estimation of effects connected with macrostresses and their influence on positions and intensities of the measured Raman peaks.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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