ULTRASONIC CHARACTERIZATION OF CERAMIC MATERIAL TITANIUM DIBORIDE

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Higher order elastic constants have been calculated in hexagonal structured ceramic material TiB$_2$ at temperature dependent following the interaction potential model. The temperature variation of the ultrasonic velocities is evaluated along different angles with z axis (unique axis) of the crystal using the second order elastic constants. The ultrasonic velocity decreases with the temperature along particular orientation with the unique axis. Temperature variation of the thermal relaxation time and Debye average velocities is also calculated along the same orientation. The temperature dependency of the ultrasonic properties is discussed in correlation with elastic, thermal and electrical properties. It has been found that the thermal conductivity is the main contributor to the behaviour of ultrasonic attenuation as a function of temperature and the responsible cause of attenuation is phonon-phonon interaction.

INTRODUCTION

Ultrasonic offer the possibility to detect and characterize microstructral properties as well as flaws in materials, controlling materials behaviour based on physical mechanism to predict future performance of the materials. Various investigators have shown considerable interest on ultrasonic properties of metals and compounds [1-4]. Wave propagation velocity is key parameter in ultrasonic characterization and can provide information about crystallographic texture. The ultrasonic velocity is directly related to the elastic constants by the relationship $V = \sqrt{(C/\rho)}$, where C is the relevant elastic constants and ρ is the density of that particular material. The elastic constants of a solid provide valuable insight into nature of atomic bonding forces and also related hardness [5, 6].

Titanium diboride (TiB$_2$) is well known as a ceramic material which presents a very attractive combination of mechanical, chemical and transport properties such as high hardness (from 20 to 30 GPa at room temperature, depending on the applied load), high melting point (about 3500 K), low density, low electrical resistivity, good thermal conductivity and excellent chemical inertness. These characteristics make it a potential candidate for several high-performance applications, in cutting tools, electrodes and wear-resistant components. Despite the prominence that TiB$_2$ has found in high-technology applications, some of its physical properties are scarcely known [7-11].

Titanium diboride is a hexagonal AlB$_2$ structure [12]. TiB$_2$ has crystallizes in the AlB$_2$ structure, space group P6/mmm, with one titanium at the origin and two boron atoms at the site 2d (1/3, 2/3, 1/2). Its structure is usually described as a simple stacking of graphite-like parallel sheets of boron intercalated with a simple hexagonal lattice of titanium, disposed in such a way that each titanium is surrounded by twelve borons, and each boron is coordinated by six Ti atoms [13].

There are several theoretical studies in the literature, involving different approaches, whose main concern is the electronic structure of the transition-metal diborides, in particular those with the AlB$_2$ structure [14-21]. However, only a few of them concern the pressure behaviour and elastic properties of these compounds. Among these, we must cite in particular van Camp and van Doren [21], who performed density functional calculations (in both local density (LDA) and generalized gradient (GGA) approximations) for TiB$_2$.

Ultrasonic attenuation is very important physical parameter to characterize the material, which is well related to several physical quantities like thermal conductivity, specific heat, thermal energy density and higher order elastic constants [22]. The elastic constants provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability [23, 24].

Therefore, in this work we predict the ultrasonic properties of hexagonal structured TiB$_2$ compound

at different temperatures. The ultrasonic attenuation coefficient, acoustic coupling constants, higher order elastic constants, thermal relaxation time and ultrasonic wave velocities for TiB$_2$ for unique direction of propagation of wave are calculated as a function of temperature. The calculated ultrasonic parameters are discussed with related thermo physical properties for the characterization of the chosen compound. The obtained results are analyzed in comparison to other hexagonal structured materials.

THEORETICAL

In the present investigation, the theory is divided into two parts:

Second-and third order elastic constants

The second (C_{IJ}) and third (C_{IJK}) order elastic constants of material are defined by following expressions.

$$C_{IJ} = \frac{\partial^2 U}{\partial e_I \, \partial e_J}; \quad I \text{ or } J = 1, \ldots\ldots 6 \qquad (1)$$

$$C_{IJK} = \frac{\partial^3 U}{\partial e_I \, \partial e_J \, \partial e_K}; \quad I \text{ or } J \text{ or } K = 1, \ldots\ldots 6 \qquad (2)$$

where, U is elastic energy density, $e_I = e_{ij}$ (i or j = x, y, z, I = 1, …6) is component of strain tensor. Equations (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal structure materials [22, 25].

$$
\begin{aligned}
&C_{11} = 24.1 \, p^4 \, C' & &C_{12} = 5.918 \, p^4 \, C' \\
&C_{13} = 1.925 \, p^6 \, C' & &C_{33} = 3.464 \, p^8 \, C' \qquad (3a) \\
&C_{44} = 2.309 \, p^4 \, C' & &C_{66} = 9.851 \, p^4 \, C'
\end{aligned}
$$

$$
\begin{aligned}
&C_{111} = 126.9 \, p^2 \, B + 8.853 \, p^4 \, C' \\
&C_{112} = 19.168 \, p^2 \, B - 1.61 \, p^4 \, C' \\
&C_{113} = 1.924 \, p^4 \, B + 1.155 \, p^6 \, C' \\
&C_{123} = 1.617 \, p^4 \, B - 1.155 \, p^6 \, C' \\
&C_{133} = 3.695 \, p^6 \, B \qquad C_{155} = 1.539 \, p^6 \, B \qquad (3b)\\
&C_{144} = 2.309 \, p^4 \, B \qquad C_{344} = 3.464 \, p^6 \, B \\
&C_{222} = 101.039 \, p^2 \, B + 9.007 \, p^4 \, C' \\
&C_{333} = 5.196 \, p^8 \, B
\end{aligned}
$$

where $p = c/a$: axial ratio; $C' = \chi \, a/p^5$; $B = \psi \, a^3/p^3$; $\chi = (1/8)[\{nb_0 \, (n-m)\}/\{a^{n+4}\}]$; $\psi = -\chi \, / \, \{6a^2 \, (m+n+6)\}$; m, n = integer quantity; b_0 = Lennard Jones parameter.

Ultrasonic attenuation and allied parameters

The predominant causes for the ultrasonic attenuation in a solid at room temperature are phonon-phonon interaction (Akhieser loss) and thermoelastic relaxation mechanisms. The ultrasonic attenuation coefficient

($Æ$)$_{Akh}$ due to phonon-phonon interaction and thermo-elastic relaxation mechanisms is given by the following expression [25, 26].

$$(Æ/f^2)_{Akh} = 4\pi^2 \, (3E_0 \, <(\gamma_i^j)^2> - <\gamma_i^j>^2 \, C_V T)\tau/2\rho V^3 \qquad (4)$$

$$(Æ/f^2)_{Th} = 4\pi^2 \, <\gamma_i^j>^2 \, kT/2\rho V_L^5 \qquad (5)$$

where f - frequency of the ultrasonic wave; V - ultrasonic velocity for longitudinal and shear wave; V_L - longitudinal ultrasonic velocity; E_0 - thermal energy density; γ_I^i - Grüneisen number (i, j are the mode and direction of propagation).

The Grüneisen number for hexagonal structured crystal along <001> orientation or $\theta = 0°$ is direct consequence of second and third order elastic constants. $D = 3(3E_0 \, <(\gamma_i^j)^2> - <\gamma_i^j>^2 \, C_V T)/E_0$ is known as acoustic coupling constant, which is the measure of acoustic energy converted to thermal energy. When the ultrasonic wave propagates through crystalline material, the equilibrium of phonon distribution is disturbed. The time for re-establishment of equilibrium of the thermal phonon distribution is called thermal relaxation time (τ) and is given by following expression:

$$\tau = \tau_S = \tau_L/2 = 3k/C_V \, V_D^2 \qquad (6)$$

where τ_L and τ_S are the thermal relaxation time for longitudinal and shear wave, k and C_V are the thermal conductivity and specific heat per unit volume of the material respectively. The Debye average velocity (V_D) is well related to longitudinal (V_L) and shear wave (V_{S1}, V_{S2}) velocities. The expressions for ultrasonic velocities are given in our previous papers [25, 26], where ρ and θ are the density of the material and angle with the unique axis of the crystal respectively. The ultrasonic velocities have been used for the calculation of ultrasonic attenuation and allied parameters in the chosen material.

RESULTS AND DISCUSSION

Higher order elastic constants

The temperature dependent unit cell parameters 'a' (basal plane parameter) 'p' (axial ratio), density and thermal conductivity (k) for TiB$_2$, are presented in Figure 1 [27]. The value of m, n and b_0 for TiB$_2$ are 6, 7 and 3.0×10^{-64} erg cm^7, respectively. The second order elastic constants (SOEC) and third order elastic constants (TOEC) have been calculated for TiB$_2$ using Equation (3) and are presented in Figures 2-3.

The elastic constants of the material are important, since they are related to hardness parameter. Also, the second order elastic constants are used for the determination of the ultrasonic attenuation and related parameters. The calculated values of C_{12}, C_{13} are few different than some other experimental [28] and theoretical [29-31] results. Actually Spoor et al. [28] were experimentally measured using resonant ultrasound
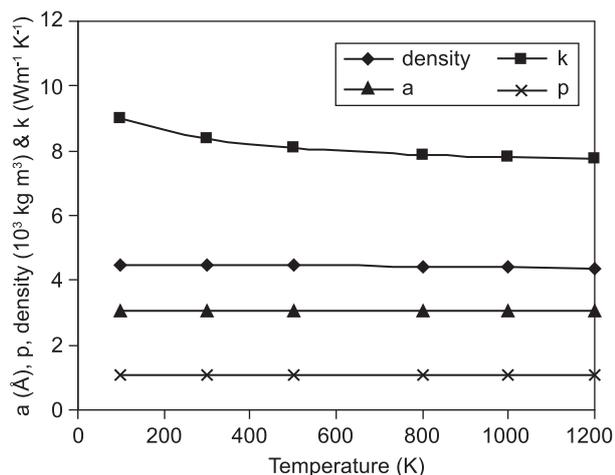
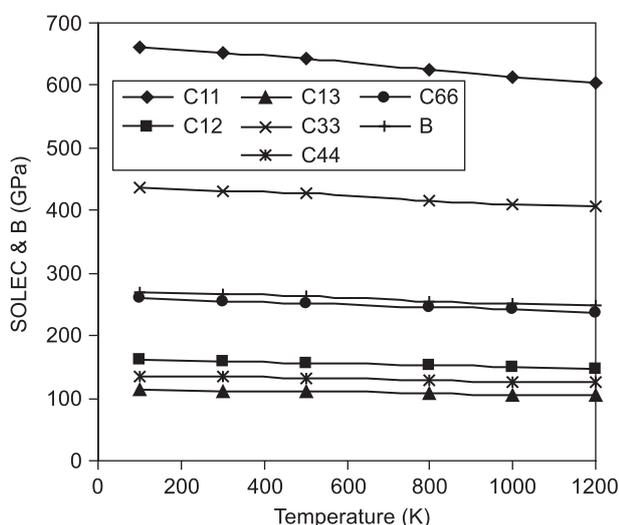Figure 1. Lattice parameters, density and thermal conductivity vs temperature.

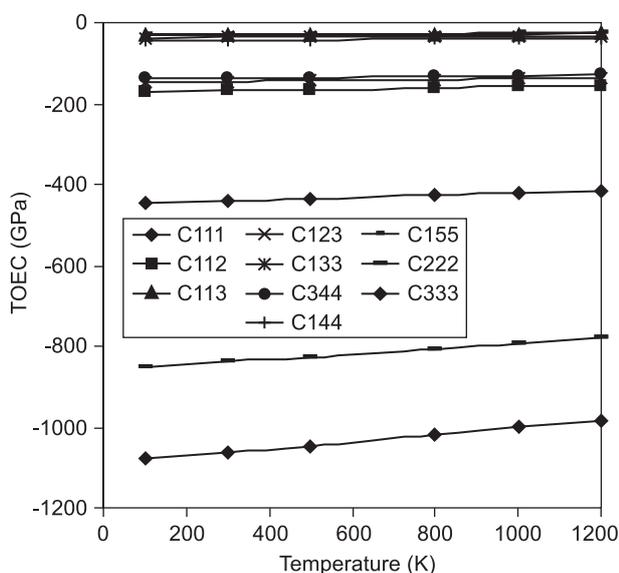Figure 2. SOEC and bulk modulus vs temperature.

Figure 3. TOEC vs temperature.

spectroscopy. Also Perottoni et al. [30] and Panda et al. [31] have based ab-initio periodic Hartree-Focke (HF) calculations to evaluate elastic constants, which is quite different from present approach. Although obtained order of SOEC are of the same as given in Table 1 [28-31]. Relative magnitude of C_{11}, C_{33}, C_{44}, C_{66} are well presented by our theoretical approach. The bulk modulus (B) for TiB$_2$ can be calculated with the formula B = 2(C_{11}+ C_{12}+ 2C_{13} + C_{33}/2)/9. The evaluated B for TiB$_2$ is presented in Table 1. It is obvious from Table 1 that, there is good agreement between the present and reported theoretical/experimental second order elastic constants and bulk modulus of TiB$_2$ [28-31]. Thus our theoretical approach for the calculation of second order elastic constants for hexagonal structured compound at room temperature is well justified. However, third order elastic constants are not compared due to lack of data in the literature but the negative third order elastic constants are found in previous papers for hexagonal structure materials [32-36]. Hence applied theory for the evaluation of higher order elastic constants at room temperature is justified.

Table 1. Comparative SOEC and bulk modulus (B) in the unit of GPa of TiB$_2$ at room temperature.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B
This work	662	163	113	438	136	260	269
Expt. [28]	660	48	93	432	260	306	240
[29]	659	62	100	461	260	299	251
[30]	786	127	87	583	271	330	299
[31]	874	130	137	444	282	372	304

Ultrasonic velocity and allied parameters

The temperature dependent density and thermal conductivity have been taken from the literature [27] which is presented in Figure 1. The value of C_V and E_0 are evaluated using tables of physical constants and Debye temperature. The values of specific heat per unit volume (C_V), thermal energy density (E_0) and calculated acoustic coupling constants (D_L & D_S) are presented in Figures 4-5.

The computed orientation dependent ultrasonic wave velocities and Debye average velocities at different temperature are shown in Figures 6-9. Figures 6-8 show that the velocities V_L and V_{S2} increases with the angle from the unique axis and V_{S1} have maxima at 45° with the unique axis of the crystal. The combined effect of SOEC and density is reason for abnormal behaviour of angle dependent velocities.

The nature of the angle dependent velocity curves in the present work is found similar as that for third group nitrides(GaN, AlN, InN), heavy rare-earth metals,

laves-phase compounds (TiCr$_2$, ZrCr$_2$, and HfCr$_2$) and other hexagonal wurtzite structured materials [32-34]. Thus the angle dependencies of the velocities in TiB$_2$ are justified.

V_D of this material is increasing with the angle and has maxima at 55° at different temperatures (Figure 9). Since V_D is calculated using V_L, V_{S1} and V_{S2} [22, 26], therefore the angle variation of V_D is influenced by the constituent ultrasonic velocities. The maximum V_D at 55° is due to a significant increase in longitudinal and pure shear (V_{S2}) wave velocities and a decrease in quasi-shear (V_{S1}) wave velocity. Thus it can be concluded that when a sound wave travels at 55° with the unique axis of this crystal then the average sound wave velocity is maximum.

The calculated thermal relaxation time is visualised in Figure 10. The angle dependent thermal relaxation time curves follow the reciprocal nature of V_D as $\tau \propto 3K/C_V V_D^2$. This implies that τ for chosen compound is mainly affected by the thermal conductivity. The τ for hexagonal structured materials is the order of pico
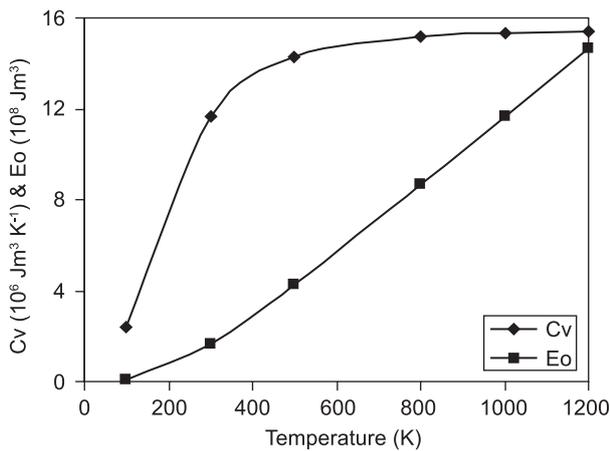

Figure 4. Specific heat per unit volume (C_V), thermal energy density (E_0) vs temperature.
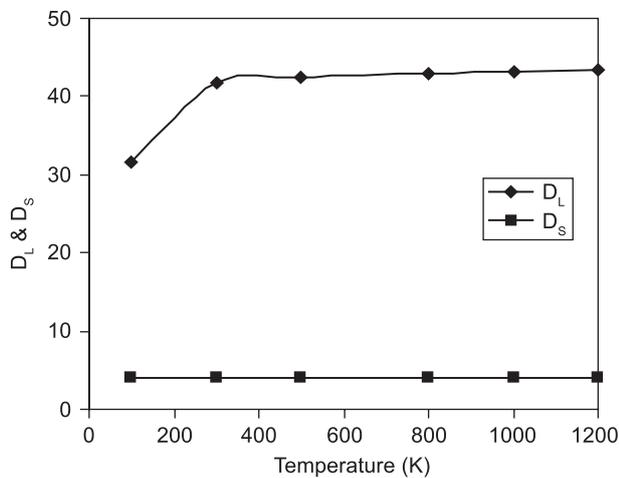

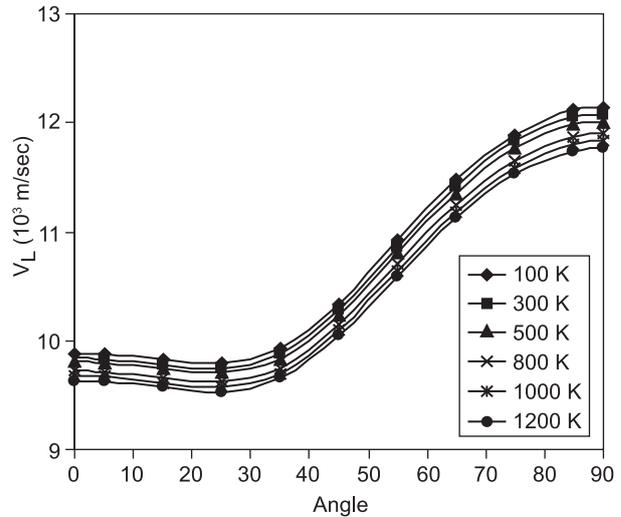Figure 5. Acoustic coupling constants vs temperature.

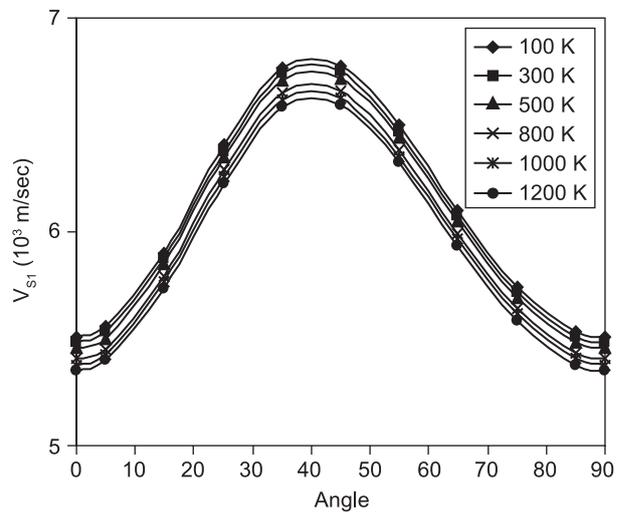Figure 6. V_L vs angle with unique axis of crystal.

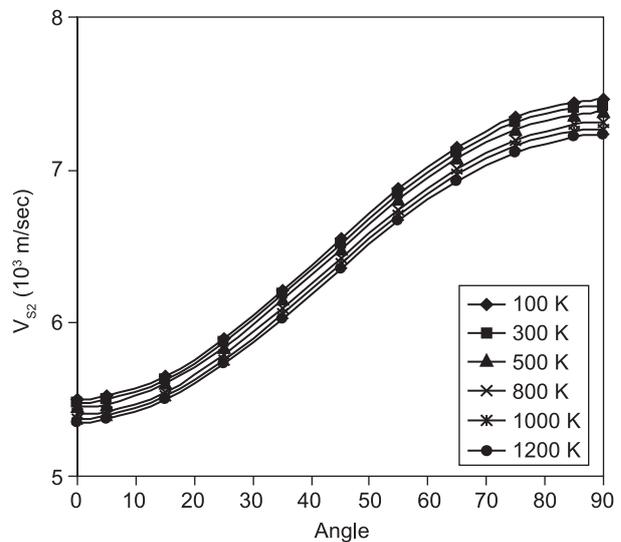Figure 7. V_{S1} vs angle with unique axis of crystal.

Figure 8. V_{S2} vs angle with unique axis of crystal.

second [34, 38, 39]. Hence the calculated τ justifies the hexagonal structure of chosen compound. The minimum τ for wave propagation along $\theta = 55^0$ implies that the re-establishment time for the equilibrium distribution of thermal phonons will be minimum for propagation of wave along this direction.

Thus the present average sound velocity directly correlates with the Debye temperature, specific heat and thermal energy density of TiB_2.

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Ultrasonic attenuation
due to phonon-phonon interaction
and thermal relaxation phenomena

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In the evaluation of ultrasonic attenuation, it is supposed that wave is propagating along the unique axis [<001> direction] of TiB_2. The attenuation coefficient over frequency square $(Æ/f^2)_{Akh}$ for longitudinal $(Æ/f^2)_L$

and shear wave $(Æ/f^2)_S$ are calculated using Equation (4) under the condition $\omega\tau \ll 1$ at different temperature. The thermoelastic loss over frequency square $(Æ/f^2)_{Th}$ is calculated with the Equation (5). The values of temperature dependent $(Æ/f^2)_L$, $(Æ/f^2)_S$, $(Æ/f^2)_{Th}$ and total attenuation $(Æ/f^2)_{Total}$ are presented in Figures 11-12.

In the present investigation, the ultrasonic wave propagates along the unique axis of the crystal, the Akhieser type of loss of energy for longitudinal and shear wave and thermo elastic loss increases with the temperature of the material (Figures 10 and 11). $(Æ/f^2)_{Akh}$ is proportional to D, E_0, τ and V^{-3} (Equations (4) and (6)). The E_0 is increasing and V is decreasing with the temperature (Figures 1-3). Hence, Akhieser loss in TiB_2 is predominantly affected by the thermal energy density E_0 and the thermal conductivity.

Therefore, the ultrasonic attenuation increases due to the reduction in the thermal conductivity. Thus ultrasonic attenuation is mainly governed by the phonon–phonon interaction mechanism. A comparison of the ultrasonic attenuation could not be made due to lack of experimental data in the literature.
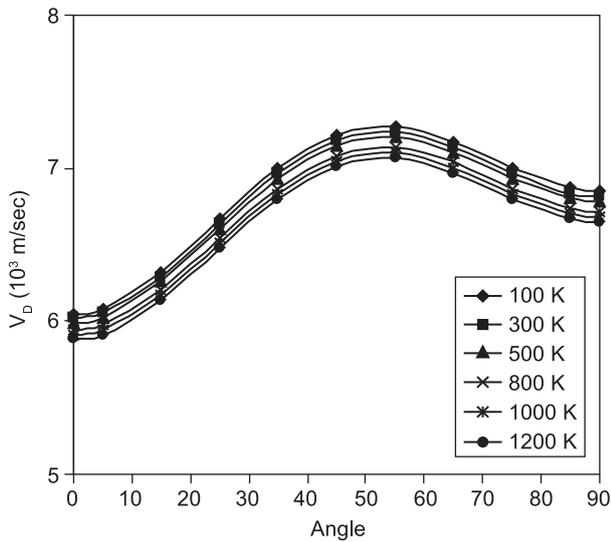
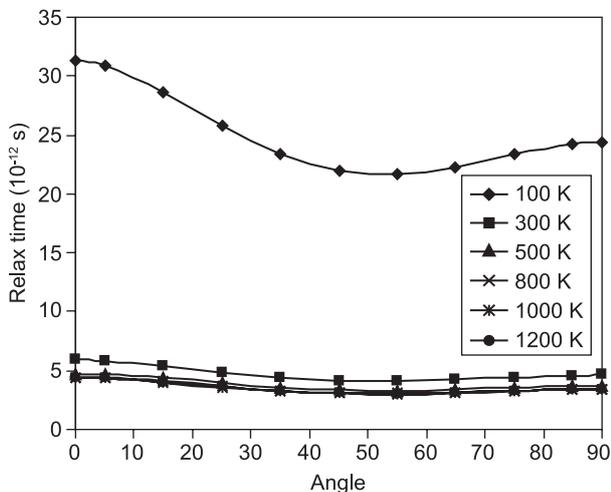Figure 9. V_D vs angle with unique axis of crystal.

Figure 11. $(Æ/f^2)_L$, $(Æ/f^2)_S$ and $(Æ/f^2)_{Total}$ vs temperature of TiB_2.
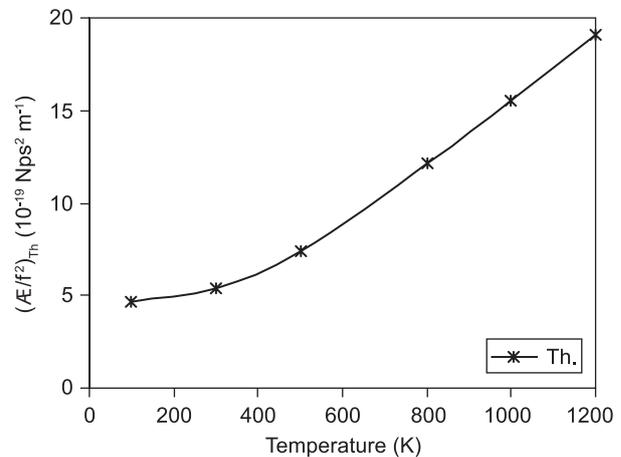
Figure 10. Relaxation time vs angle with unique axis of crystal.

Figure 12. $(Æ/f^2)_{Th}$ vs temperature of TiB_2.

Figures 11-12 indicate that the thermoelastic loss is very small in comparison to Akhieser loss and ultrasonic attenuation for longitudinal wave $(Æ/f^2)_L$ is greater than that of shear wave $(Æ/f^2)_S$. This reveals that ultrasonic attenuation due to phonon-phonon interaction along longitudinal wave is governing factor for total attenuation $((Æ/f^2)_{Total} = (Æ/f^2)_{Th} + (Æ/f^2)_L + (Æ/f^2)_S)$. The total attenuation is mainly affected by thermal energy density and thermal conductivity. Thus it may predict that at lower temperature (100 K) the TiB_2 behaves as its purest form and is more ductile as evinced by minimum attenuation while at higher temperature TiB_2 is least ductile. Therefore impurity will be least in the TiB_2 at lower temperature.

Since $Æ \propto V^{-3}$ and velocity is the largest for TiB_2 at lower temperature (100 K) among TiB_2 at higher temperature (1200 K) thus the attenuation A should be smallest at lower temperature and material should be most ductile. The minimum ultrasonic attenuation for TiB_2 at lower temperature (100 K) justifies its quite stable hexagonal structure state. The total attenuation of TiB_2 is much larger than third group nitrides (AlN: 4.441×10^{-17} Nps²m⁻¹; GaN: 14.930×10^{-17} Nps²m⁻¹ and InN: 20.539×10^{-17} Nps²m⁻¹) due to their large thermal conductivity and acoustic coupling constants [34, 35]. This implies that the interaction between acoustical phonon and quanta of lattice vibration for TiB_2 is large in comparison to third group nitrides.

CONCLUSIONS

On the basis of above discussion, we conclude following points:

- Our theory of higher order elastic constants is justified for the hexagonal structured material.
- The thermal relaxation time for hcp structured material follows the equation $\tau = \tau_0 \exp(x/\lambda)$, where x and λ are constants. The order of τ for hexagonal structure in picoseconds. With reference some previous work [38, 39], the size dependency of τ for bcc and fcc structured materials follow the equation $\tau = \tau_0 [1- \exp(-x/\lambda)]$. Thus it can be said that the thermal relaxation time is not only function of size and temperature but also depends on the structure of a materials. The order of thermal relaxation time for TiB_2 is found in picoseconds, which justifies their hexagonal structure. The re-establishment time for the equilibrium distribution of thermal phonons will be minimum for the wave propagation along $\theta = 55°$ due to being smallest value of τ along this direction.
- The acoustic coupling constant of TiB_2 for longitudinal wave are found five times larger than third group nitrides. Hence the conversion of acoustic energy into thermal energy will be large for TiB_2. This shows general suitability of chosen material comparison than third group nitrides.

- The ultrasonic attenuation due to phonon-phonon interaction mechanism is predominant over total attenuation as a governing factor thermal conductivity.
- The mechanical properties of TiB_2 at lower temperature (100 K) are better than at higher temperature (1200 K), because at low temperature it has high SOEC, ultrasonic velocity and low ultrasonic attenuation.

Thus obtained results in the present work can be used for further investigations, general and industrial applications. Our theoretical approach is valid for temperature dependent ultrasonic characterization of TiB_2. Thus the whole theoretical approach can be applied to the evaluation of ultrasonic attenuation and related parameters to study the microstructural properties of hcp TiB_2 compound. These results, together with other well-known physical properties, may expand future prospects for the application and study of TiB_2.

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