Elastic and Acoustic Properties of XB_2 (X= V, Nb & Ta) Transition Metal Diborides

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Abstract The elastic properties, acoustic properties and mechanical properties of the group VB transition metal diborides like VB_2, NbB_2 and TaB_2 have been studied along unique axis at room temperature. The second- and third order elastic constants (SOEC & TOEC) have been calculated for these diborides using Lennard–Jones potential model. The velocities V_L and V_{S2} increases with the angle from the unique axis and V_{S1} have maximum at 45° with unique axis of the crystal. The inconsistent behaviour of angle dependent velocities is associated to the action of second order elastic constants. Debye average sound velocities of these compounds are increasing with the angle and has maximum at 55° with unique axis at room temperature. Hence when a sound wave travels at 55° with unique axis of these materials, then the average sound velocity is found to be maximum. The mechanical properties of VB_2 are better than TaB_2, because VB_2 has low ultrasonic attenuation comparison than TaB_2. The diborides are good electrical conductors; they are attractive for the same types of applications as other hard refractory materials such as in composite and in hard coating. Traditional applications o such materials are based on their interesting combination of mechanical and transport properties.

Keywords: elastic properties, VB transition metal diborides, thermal conductivity, acoustic properties

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1. Introduction

VB transition metal diborides are interest for fundamental reasons as well as for practical applications. Borides of transition metals have various unique properties which in many cases are of great importance from technological view points. Among their attractive properties are high thermal and chemical stability, high electrical and thermal conductivity, and high hardness and high mechanical stiffness [1]. VB transition metal diborides XB_2 (X= V, Nb and Ta) with the hexagonal structure have attracted much attention because of its physical and chemical properties such as wear resistance, corrosion resistance, high hardness, high melting point and oxidation, and extensive industrial applications [2,3,4,5,6].

Ultrasonics techniques are widely used for the determination of elastic properties and the characterization of the microstructure of materials. The elastic constants are determined by the measurement of velocities of the longitudinal and shear waves [7], while the microstructure is generally evaluated by measuring their attenuation [8]. Ultrasonic also offers the possibility of measuring texture [9,10], phase change and residual stresses [11]. Ultrasonic velocity and attenuation has been shown also to correlate in certain cases to fracture toughness and fatigue damage [12]. Recently ultrasonic velocity and attenuation has been studied in various physical states and conditions.

There are three types of acoustic mode lattice vibration: one longitudinal acoustic and two transverse acoustical for hexagonal and cubic structured materials [13,14]. Hence, there are three types of acoustic wave velocities for each direction of propagation of wave, which are well related to second order elastic constants. But all the three type of orientation dependent acoustic wave velocity of these all materials are not reported in literature. Therefore in this paper, we predict the ultrasonic properties of hexagonal structured VB_2, NbB_2 and TaB_2 at room temperature. The ultrasonic attenuation coefficient, acoustic coupling constants, higher order elastic constants, thermal relaxation time and ultrasonic wave velocities for these diborides for each direction of propagation of wave are calculated at room temperature. The calculated ultrasonic parameters are discussed with related thermophysical properties for the characterization of the chosen compounds. The obtained results are interesting for characterization of these diborides materials.

2. Theory

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

2.1. Second and Third Order Elastic Constants

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

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

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

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 close packed structure materials [15,16].

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

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

where $p = c/a$: axial ratio; $C' = \chi\,a\,/\,p^5$; $B = \psi\,a^3\,/\,p^3$;

$\chi = (1/8)[\{nb_0\,(n-m)\}/\{\,a^{n+4}\}]$

$\psi = -\chi\,/\{6\,a^2(m+n+6)\}$; m, n=integer quantity; b_0=Lennard Jones parameter.

2.2. 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 $(A)_{Akh}$ due to phonon-phonon interaction and thermoelastic relaxation mechanisms is given by the following expression [17,18].

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

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

where, f: frequency of the ultrasonic wave; ρ :the density of the material V: ultrasonic velocity for longitudinal and shear wave; V_L: longitudinal ultrasonic velocity; E_0:

thermal energy density; γ_i^j: Grüneisen number (i, j are the mode and direction of propagation).

The Grüneisen number for hexagonal structured crystal along <001> orientation or $\theta=0^0$ is direct consequence of second and third order elastic constants. $D = 3\left(3E_0 <(\gamma_i^j)^2> - <\gamma_i^j>^2 C_V T\right)/E_0$ 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:

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

Here 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 paper [16].

3. Results & Discussion

3.1. Higher Order Elastic Constants

The unit cell parameters 'a' (basal plane parameter) and 'p' (axial ratio) for VB$_2$, NbB$_2$ and TaB$_2$ are 2.993Å, 3.107Å, 3.104Å and 1.012, 1.067, 1.133 respectively [19]. The value of m and n for chosen materials are 6 and 7. The values of b_0 are 2.5x10^{-64} erg cm^7, 4.0x10^{-64} and 3.0x10^{-64} erg cm^7 for VB$_2$, NbB$_2$ and TaB$_2$ respectively. The SOEC and TOEC have been calculated for these compounds using equation. (3) and bulk modulus (B) are presented in Table 1.

Table 1. Second and third order elastic constants (SOEC and TOEC) & Bulk Modulus (B) in the unit of GPa of VB$_2$, NbB$_2$ and TaB$_2$ compounds at room temperature

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B
VB$_2$	678	118	129	472	231	232	287
NbB$_2$	599	132	187	449	228	212	295
TaB$_2$	505	196	240	434	162	217	311
[19] VB$_2$	678	119	131	471	228		284
[19] NbB$_2$	594	132	170	468	236		288
[19] TaB$_2$	489	195	232	434	145		305

The elastic constants of the material are important, since they are related to hardness and therefore of interest in applications where mechanical strength and durability are important. Also, the second order elastic constants are used for the determination of the ultrasonic attenuation and related parameters. It is obvious from Table 1 that, there is good agreement between the present and reported theoretical and experimental second order elastic constants and bulk modulus of VB$_2$, NbB$_2$ and TaB$_2$ [19]. The bulk modulus (B) for these compounds can be calculated with the formula B= 2(C_{11}+ C_{12}+ 2C_{13} + C_{33}/2)/9 [20]. Hence applied theory for the evaluation of higher order elastic constants at room temperature is justified.

3.2. Ultrasonic Velocity and Allied Parameters

The density and thermal conductivity at room temperature have been taken from the previous works [21,22,23]. The value of C_V and E_0 are evaluated using tables of physical constants and Debye temperature. The quantities ρ, C_V and E_0, 'k' and calculated acoustic coupling constants (D_L and D_S) are presented in Table 2.

Table 2. Density (ρ: in 10^3 kg m^{-3}), specific heat per unit volume (C_V: in 10^6 Jm^{-3} K^{-1}), thermal energy density (E_0: in 10^8 Jm^{-3}), thermal conductivity (k: in Wm^{-1} K^{-1}) and acoustic coupling constant (D_L, D_S) of VB$_2$, NbB$_2$ and TaB$_2$ compounds

Compounds	ρ	C_V	E_0	k	D_L	D_S
VB$_2$	5.07	1.32	1.89	42.30	53.47	3.06
NbB$_2$	6.97	1.28	2.02	20.25	55.73	1.55
TaB$_2$	12.54	1.38	2.52	13. 45	56.14	1.51

The calculated orientation dependent ultrasonic wave velocities and Debye average velocities at room temperature are shown in Figure 1–Figure 4. Figure 1–Figure 3 show that the V_L and V_{S2} increases with the angle from the unique axis and V_{S1} have maximum at 45^0 with unique axis of the crystal. The combined effect of SOEC and density is cause for abnormal behaviour of angle dependent velocities.
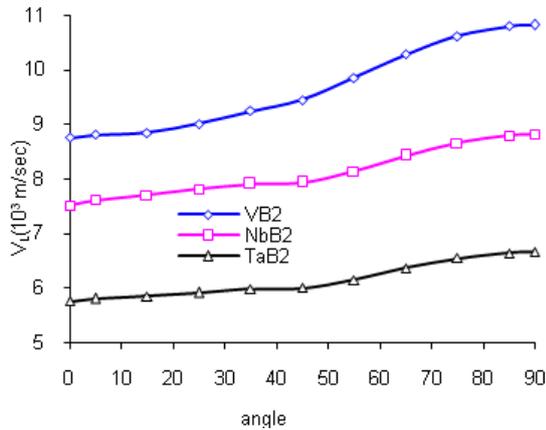
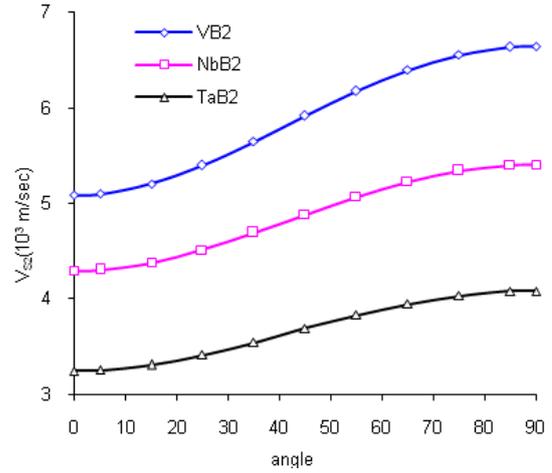**Figure 1.** V_L vs angle with unique axis of crystal
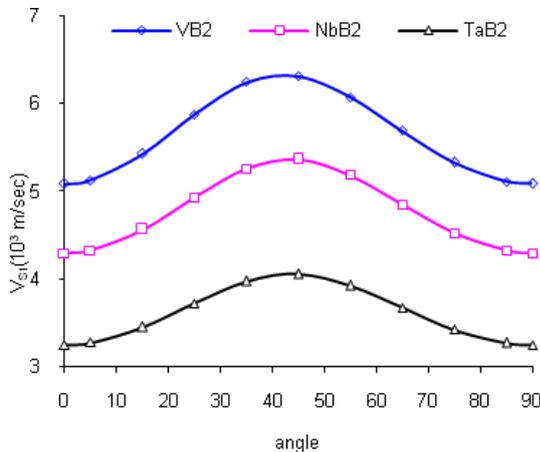
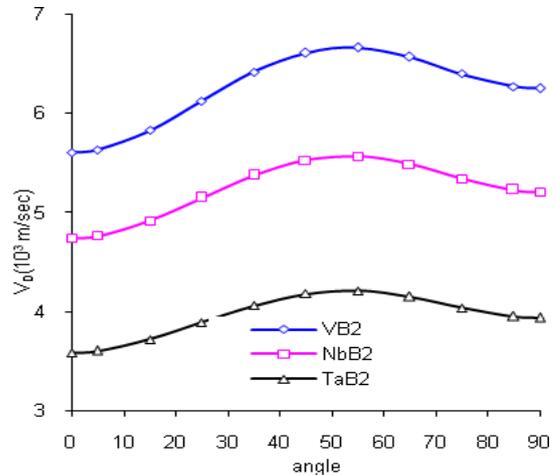**Figure 2.** V_{S1} vs angle with unique axis of crystal

The nature of the angle dependent velocity curves in the present work is found similar as that for other hexagonal

diborides materials [20,24]. Thus the computed velocities for these materials are justified.

Debye average velocities (V_D) of these compounds are increasing with the angle and have maxima at 55° at 300 K (Figure 4). Since V_D is calculated using V_L, V_{S1} and V_{S2} [24], 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 these materials then the average sound wave velocity is maximum.

Figure 3. V_{S2} vs angle with unique axis of crystal

Figure 4. V_D vs angle with unique axis of crystal

The thermal relaxation time for hexagonal structured material follows the equation $\tau = \tau_o \exp(x/\lambda)$, where '$\tau$' and '$\lambda$' are constants. The order of 'τ' for hexagonal structure diborides is in picoseconds [20]. With reference some previous work [25,26], the size dependency of 'τ' for bcc and fcc structured materials follow the equation $\tau = \tau_o [1- \exp(-x/\lambda)]$. 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. Hence the calculated τ justifies the hexagonal structure of chosen compounds at room temperature. 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.
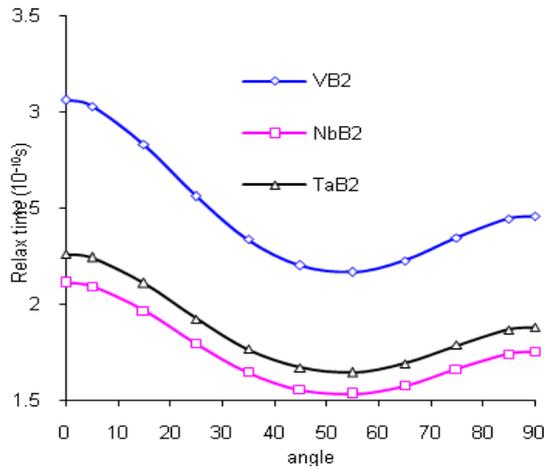

Figure 5. Relaxation time vs angle with unique axis of crystal

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

3.3. Ultrasonic Attenuation

In the evaluation of ultrasonic attenuation, it is supposed that wave is propagating along the unique axis (<001> direction) of these metals. The attenuation coefficient over frequency square $(A/f^2)_{Akh}$ for longitudinal $(A/f^2)_L$ and shear wave $(A/f^2)_S$ are calculated using Equation (4) under the condition $\omega\tau \ll 1$ at room temperature. Thermoelastic loss over frequency square $(A/f^2)_{Th}$ is calculated with the Equation (5). The values of $(A/f^2)_L$, $(A/f^2)_S$, $(A/f^2)_{Th}$. and total attenuation $(A/f^2)_{Total}$ are presented in Table 3.

Table 3. Ultrasonic attenuation coefficient (in 10^{-18} Nps^{2}m^{-1}) of VB$_2$, NbB$_2$ and TaB$_2$ compounds

Alloys	VbB_2	NbB_2	TaB_2
$(A/f^2)_{Th}$	0.21	0.32	0.41
$(A/f^2)_L$	156.71	189.21	270.56
$(A/f^2)_S$	15.69	24.91	26.31
$(A/f^2)_{Total}$	172.61	214.44	297.28

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 (Table 3). $(A/f^2)_{Akh}$ 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 (Figure 1-Figure 3). Hence, Akhieser loss in these compounds 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.

Table 3 indicate that the thermoelastic loss is very small in comparison to Akhieser loss and ultrasonic

attenuation for longitudinal wave $(A/f^2)_L$ is greater than that of shear wave $(A/f^2)_S$. This reveals that ultrasonic attenuation due to phonon-phonon interaction along longitudinal wave is governing factor for total attenuation $((A/f^2)_{Total} = (A/f^2)_{Th} + (A/f^2)_L + (A/f^2)_S)$. The total attenuation is mainly affected by thermal energy density and thermal conductivity. Thus it may predict that at room temperature VB$_2$ behaves as its purest form and is more ductile as evinced by minimum attenuation comparison than TaB$_2$.

Since ultrasonic attenuation $(A) \propto V^{-3}$ and ultrasonic velocity is the largest for VB$_2$ compound among TaB$_2$ compound thus the attenuation (A) have smallest for VB$_2$ and material should be most ductile. The minimum ultrasonic attenuation for VB$_2$ justifies its quite stable hexagonal structure state. The attenuation of these diborides is smaller than other diborides compounds (TiB$_2$, MnB$_2$, TcB$_2$, ReB$_2$ and OsB$_2$) due to their smaller velocities [20,24,27]. This implies that the interaction between acoustical phonon and quanta of lattice vibration for these VB transition metal diborides is smaller in comparison to other group diborides.

4. Conclusions

Present method to evaluate second and third order elastic constants involving much body interaction potential for hexagonal structured VB transition metal diborides compounds is correct. All elastic constants and density are mainly the affecting factor for anomalous behaviour of ultrasonic velocity in these compounds. The order of thermal relaxation time for these compounds 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 $\theta = 55^0$ due to being smallest value of τ along this direction. The acoustic coupling constant of these group compounds for longitudinal wave are found larger than other group diborides. Hence the conversion of acoustic energy into thermal energy will be large for these compounds. The ultrasonic attenuation due to phonon-phonon interaction mechanism is predominant over total attenuation as a governing factor thermal conductivity.

The mechanical properties (yield strength, ductility, elastic properties) of VB$_2$ are better than TaB$_2$, because at VB$_2$ has high ultrasonic velocity and low ultrasonic attenuation. The results obtain in this investigation can be used for further study of these transition metal diborides. Our whole theoretical approach can be applied to the evaluation of ultrasonic attenuation and related parameters to study the michrostructural properties of hexagonal structured materials.

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