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High pressure behavior of TiX (X = C, N, O) compounds

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In the paper are calculated the structural and elastic properties of TiC, TiN and TiO at high pressure by using a two-body interionic potential theory that includes the effect of Coulomb screening. The calculated values for the bulk modulus and elastic constants are mostly in very good agreement in experiments. There were also reported the second and third order elastic constants and second order pressure derivatives. They demonstrate the predominantly ionic nature of these compounds. It is predicted that at high pressures these compounds undergo a structural phase transition from the NaCl structure into the more dense CsCl atomic configuration.

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1. Introduction

The transition metal compounds (MX) where the M denotes transition metal element Ti and X denotes non-metallic elements C, N and O, are refractory-metal compounds. The carbides and nitrides of Ti are ultra hard materials (compared to diamond) and crystallize in the rocksalt structure. Their high melting point, hardness, brittleness and metallic conductivity are common to all carbides and nitrides of the group IV and V transition metals [1]. It is interesting that the properties associated with covalent bonding are found in a set of systems which display a crystal structure normally associated with ionic bonding (NaCl). The type of bonding found for the MX systems is not typically ionic but as shown in ref.[2] more covalent and it occurs an ionic-like structure in combination with covalent-like. TiN is presently one of the most important materials for hardness and corrosion resistant coating material. Interest is also developing within the microelectronic industry for the use of TiN as an electrically conducting barrier. The relative position and degree of admixture of the 2s and 2p metalloid levels with the d and s transition-metal states play a decisive role in the binding. Several models favoring metal-metal or metal-nonmetal interaction have been proposed [3-5] to account for the trends in the properties of these compounds. The orbital overlap and the character of the d band in the transition metal oxides have been analyzed by Morin and Goodenough [6,7]. Other authors [5,8,9] have investigated the stability of the rocksalt structure in the hard metals, in particular the vacancy problem in TiO. The local-density approximation (LDA) within the density functional theory (DFT) has been used to calculate electronic and ground state properties of these compounds. This approach works for most systems like for the 3d transition metals, but it underestimates the bulk modulus [10,11]. To remove these drawbacks they proposed approximations referred to as PW91 [12]. This gives considerable improvement of the ground state properties of many atomic, molecular and solid-state systems [13].

This way Ozolins and Körling performed calculation based on full potential linear muffin-tin orbital (FPLMTO) method using PW91, for explaining the structural and cohesive properties of transition metals. Unfortunately there was a lack of elastic constants calculations using the GGA and was not concluded whether or not the GGA reproduce this quantity better than LDA. Fermi surface for the noble metals [14] using a full potential linear muffin-tin orbital method (FP LMTO) within LDA was also calculated for further improvement. In this paper we made calculations based on the interaction theory with the purpose to continue to find to what extent two-body inter-ionic theory calculations improve the results for the structural and elastic properties of solid state systems.

The study of the 3-D structure of these materials is an interesting and important step for understanding their basic properties. We have determined the equilibrium lattice constants, bulk moduli, and cohesive energies for these materials. Zhukov overestimated the equilibrium volumes for TiN, TiO and their calculated values of the bulk moduli for TiC and TiN are very large in comparison to experimental values. Price et al. [15] have studied the electronic structure, total energies, equilibrium lattice constants, bulk moduli and fracture properties of stoichiometric TiC using the full potential linear muffin-tin orbitals (LMTO) method with LDA approximation for the exchange-correlation potential. Häglund et. al [16] have studied the bonding properties of transition metal carbides and nitrides. On the experimental side there are also a lot of recent efforts to study the hardness and elastic properties of TiN using different techniques such as Brillouin scattering and depth-sensing indentation [17], as well as by continuous indentation technique [18] and by line–focus acoustic microscopy [19]. The lack of data on the behaviour under high pressure motivated us to investigate the structural, elastic and high pressure properties of TiX compounds.

The rest of the paper is organized as follows. In sec. II we describe the details of the calculations and in sec. III we discuss our results for the 3-D structure, lattice stability and elastic constants of second and third order, inter-ionic distance with pressure, high pressure structural phase stability and shear modulus, young modulus, Poisson's ratio discuss first time in this paper.

2. Method of calculation

The interionic potential for transition metal mononitrides compounds in the rigid ion approximation is expressed as [21]:

$$U(r) = \sum_{ij} \frac{z_m^2 e^2}{r_{ij}} + \sum_{ij} b\beta_{ij} \exp\left[\frac{r_i + r_j - r_{ij}}{\rho_{ij}}\right] + \sum_{ij} \frac{c_{ij}}{r_{ij}^6} + \sum_{ij} \frac{d_{ij}}{r_{ij}^8} \quad (1)$$

where, $Z_m e$ is the modified ionic charge due to screening of 3d electrons of the transition metal ions. In eq (1) the first term is the long range Coulomb, second term represents the short range repulsive, third and fourth terms are the Van der Waals interaction energies, respectively. r_{ij} is the nearest neighbour separation between the ions; r_i and r_j are the ionic radii. Such an interionic potential has been found extremely useful in studying the structural and high-pressure properties of several rare-earth pnictides [21-23]. The short range parameters b and ρ have been determined self consistently from bulk modulus, B_T and the equilibrium condition

$$\left|\frac{dU(r)}{dr}\right|_{r=r0} = 0 \quad (2)$$

Here r_0 is equilibrium lattice constant. Thermodynamically a phase transition is said to occur when changes in the structural details of the phase are caused by a variation of the free energy. These compounds transform from their initial NaCl to CsCl structure under pressure. The stability of a particular structure is decided by the minima of the Gibbs free energy, given by

$$G=U+PV-TS \quad (3)$$

where, U is the internal energy (Eq.1) which at 0 K corresponds to the cohesive energy, S is the vibrational entropy at absolute T, pressure P, and volume V. The Gibbs free energies, $G_{B1}(r)$ for NaCl (B_1), and $G_{B2}(r')$ for CsCl (B_2) phases become equal at the phase transition pressure P_t at temperature 0 K. In the present paper, we have studied the high pressure properties of the B_2 phase only and calculated the second order elastic (SOE) constants from the following expressions, derived from the interionic potential [eq. (1)] as:

$$C_{11} = \alpha[-5.112\ Z_m{}^2 + A_1 + 1/2\ (A_2 + B_2)] \quad (4)$$

$$C_{12} = \alpha[0.226\ Z_m{}^2 - B_1 + 1/4\ (A_2 - 5B_2)] \quad (5)$$

$$C_{44} = \alpha[2.556\ Z_m{}^2 + B_1 + 1/4\ (A_2 + 3B_2)] \quad (6)$$

where $\alpha = e^2 / 4r_0^4$

and, $A_1 = A_{12}$, $B_1 = B_{12}$, $A_2 = (A_{11}+A_{22})$ and $B_2 = (B_{11}+B_{22})$, are short range force constants and are expressed as:

$$\left.\begin{aligned} A_{ij} &= 2V/e^2\,[d^2\phi_{ij}(r)/dr^2] \\ B_{ij} &= 2V/e^2\,[1/r_{ij}(d\phi_{ij}(r)/dr)] \end{aligned}\right\} \quad (7)$$

where $\phi_{ij}(r)$ is the short range potential (last three terms) in eq (1) and *V* is the unit cell volume. The expressions for the third order elastic constants (TOEC) can be derived as follows

$$C_{111} = \alpha\,[37.556\ Z_m{}^2 + C_1 - 3A_1 + 1/4\,(C_2 - 3A_2 - 9B_2)]$$
$$C_{112} = C_{166} = \alpha\,[-4.786\ Z_m{}^2 + 1/8\,(C_2 - 3A_2 - 3B_2)] \quad (8)$$
$$C_{123} = C_{144} = C_{456} = \alpha\,(2.717\ Z_m{}^2)$$

with $C_{1(2)} = A^2_{1(2)} / B_{1(2)}$. The expressions for the pressure derivatives of second order elastic constants can be derived from the combination of $SOEC_s$ and $TOEC_s$ constants may be evaluated for the two models and are calculated as

$$\frac{dB}{dP} = -\ 1/3\ (C_{111} + 6C_{112} + 2C_{123}) / C_{11} + 2C_{12}$$
$$\frac{dC_{44}}{dP} = -\ (C_{11} + 2C_{12} + C_{44} + C_{144} + 2C_{166}) / C_{11} + 2C_{12} \quad (9)$$
$$\frac{dG}{dP} = -\ 1/2\ (3C_{11} + 3C_{12} + C_{111} - C_{123}) / C_{11} + 2C_{12}$$

The expressions for the shear moduli C_{44} or G can be written as

$$C_{44} = G = (C_{11} - C_{12}) / 2 \quad (10)$$

Here, G represent the shear modulus and E is the Young modulus calculated using the formula

$$E = (C_{11}-C_{12})\,(C_{11}+2C_{12})/(C_{11}+C_{12}). \quad (11)$$

We use these two relations to calculate the Poisson ratio

$$\sigma = C_{12} / (C_{11}+C_{12}). \quad (12)$$

3. Results and discussion

First we analyze the input crystal properties and model paramater of the binary transition metal carbides, nitrides and oxides, all results are shown in Table1. Our calculated values for the equilibrium lattice constants and bulk moduli B_T for the TiC, TiN and TiO together with experimental and theoretical values are summarized in Table 1.

Table 1. Input crystal properties and model parameter for TiX compounds.

Solids	Input Parameters					Output Parameters	
	r_{1+} (Å)	r_{2-} (Å)	r_0 (Å)	B_T (Mbar)	Z_m^2	b (10^{-19}J)	ρ (Å)
TiC	1.13	1.03	2.16	2.42	2.55	0.854	0.206
TiN	1.13	0.99	2.12	2.88	3.24	1.162	0.225
TiO	1.13	0.93	2.09	2.70	2.45	0.998	0.200

In Table 2 lattice constants in NaCl (B_1) and in CsCl (B_2) phases, cohesive energies, phase transition pressure and volumes are presented. The values of lattice constants and cohesive energies in NaCl structure indicate that these compounds are more stable in NaCl phase than in CsCl phase. The calculated values of transition pressures indicate that these transition metal nitrides (TMN), in general, transform to CsCl phase at a pressure 57 GPa, 126 GPa and 79 GPa for TiC, TiN and TiO, respectively. The equation of state for transition metal compounds (TiC, TiN and TiO) have been calculated up to various pressure ranges and plotted in Fig. 1. N. A. Dubrovinskaia et al. [24] have observed a phase transformation from the NaCl type cubic structure (B_1) to a rhombohedral structure at pressure above 18 GPa at 300 K under quasi-hydrostatic environment. This rhombohedral structure is the intermediate structure of NaCl (B_1) to CsCl (B_2). But the graph of TiC between relative volume (V/V_0) vs pressure (GPa) shown in Ref. [24] does not satisfy us. This curve does not satisfy the accurate condition of phase transformation. We have calculated phase transition of TiC, TiN and TiO from cubic NaCl (B_1) to CsCl (B_2) phase under pressure of 57 GPa, 126 GPa and 79 GPa, respectively.

Fig. 2 shows the variation of Ti-C, Ti-N and Ti-O and C-C, N-N and O-O distance with pressure for three compounds. In TiC the distance between Ti and C ion is 2.17 Å at ambient pressure. The Ti-C distance is slightly shorter than the sum of the atomic radius of Ti (2.00 Å) and atomic radius of C (0.91 Å), but longer than the sum of covalent radii of Ti (1.32 Å) and C (0.77 Å). Thus chemical bond between Ti and C atoms are predicted to be partially covalent in nature. At NaCl (B_1) to CsCl (B_2) transition pressure the Ti-C distance suddenly increases and becomes 2.27 Å in the CsCl phase. In the similar manner the distance between C-C ions first decreases with pressure but abruptly decreases at transition pressure in CsCl structure. The same analysis has been done for the other two compounds TiN and TiO and found satisfactory explanation.

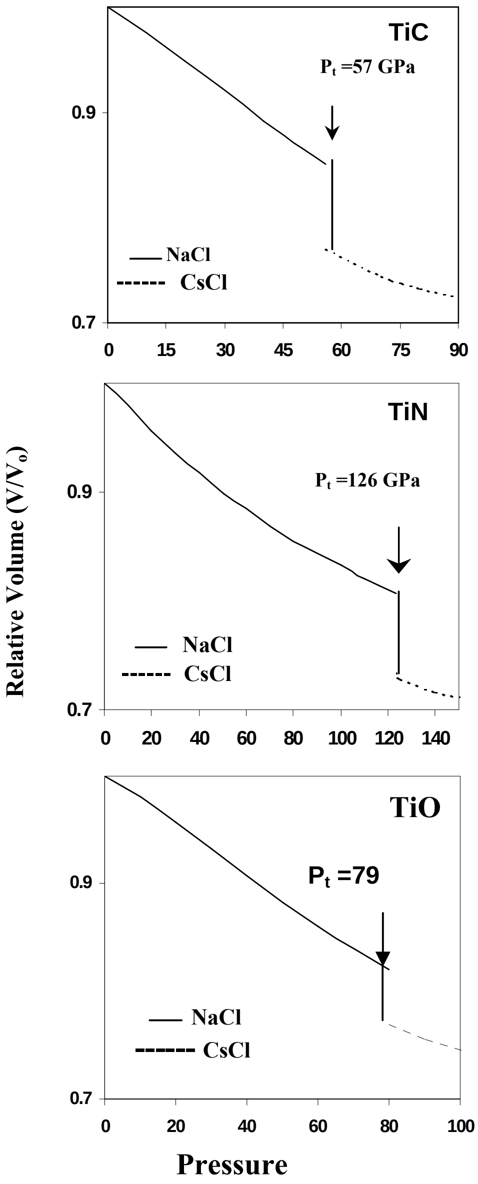

Fig. 1. Equation of state for TiC, TiN and TiO.

Table 2. Cohesive and phase properties of TiX compounds

Solids		Equillibium lattice constant (Å)	Cohesive energy (kJ/mole)	Phase transition pressure (P_t) (GPa)	Relative volume change %
		$R_1(B_1)$ $R_2(B_2)$	$U_1(B_1)$ $U_2(B_2)$		
TiC	Present	2.1798 2.2725	-2616.2 -2544.6	57	9.6
	Expt.	2.16[a]			
TiN	Present	2.1386 2.2519	-3338.2 -3222.4	126	7.3
	Expt.	2.12[a]			
TiO	Present	2.1077 2.2107	-2597.2 -2517.1	79	9.0
	Expt.	2.09[a]			

[a]Ref. [14]

The determination of the elastic constants requires the knowledge of the curvature of the energy curve as a function of strain for selected deformations of unit cell. Some of these deformations change the volume of the unit cell, but maintain the tetragonality symmetry, whereas other deformations break the tetragonality. The formulas and procedures for the calculations of the elastic constants, phase transition and Poisson's ratios are given and discussed in this paper.

Table 3. Calculated and experimental elastic constants (Mbar) of TiX compounds.

Solids	C_{11}			C_{12}			C_{44}			B_T		
	Expt	Theo	LDA	Expt	Theo	LDA	Expt	Theo	LDA	Expt	Theo	LDA
TiC	5.13[a]	5.12	6.06[a]	1.06[a]	1.00	1.06[a]	1.78[a]	1.00	2.3[a]	2.42[a]	2.38	2.7[a]
TiN	6.25[a]	5.37	7.35[a]	1.65[a]	1.44	0.93[a]	1.63[a]	1.44	2.5[a]	2.88[a]	2.73	3.1[a]
TiO	-	5.56	6.93[a]	-	1.15	0.73[a]	-	1.15	1.3[a]	2.70[a]	2.62	2.8[a]

[a] Ref. [14]

Our theoretical calculations of elastic constant C_{ij} for binary compounds TiC, TiN and TiO compared to the LDA (GGA) and experiment are listed in Table 3. A comparison of the elastic constants with the experimental values is fairly limited. Since the bulk modulus is inversely proportional to the bond length, the smaller atomic size of carbon, nitrogen and oxygen and the shorter bond length in these materials cause the bulk modulus to be larger, and consequently the elastic constants, which in turn are related to hardness, are larger in this family of compounds. Our results show that the elastic constant C_{44} is higher for TiN than for TiC and TiO. We see that our calculated theoretical values of the elastic constants are lower than the experimental and LDA values.

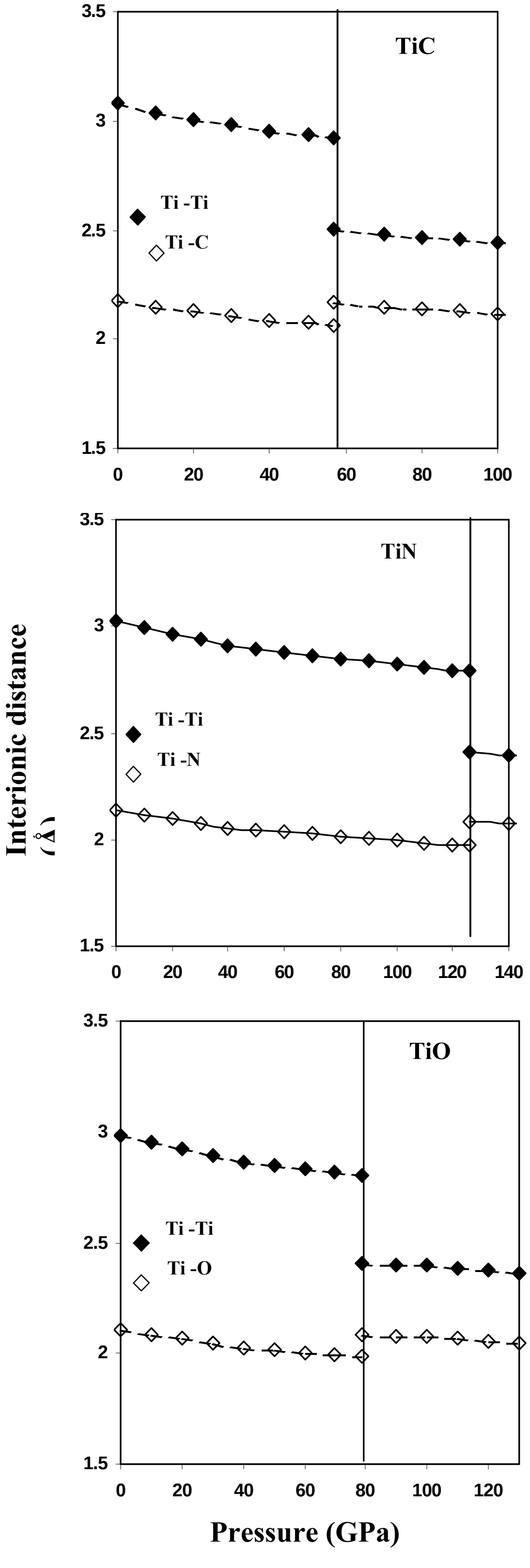

Fig. 2. Ti-Ti and Ti-X distance vs pressure curves for TiC, TiN and TiO.

Table 4. Third order elastic constants and pressure derivatives of second order elastic constants.

Solids	C_{111}	$C_{112}=C_{116}$	$C_{123}=C_{144}=C_{456}$	K_P	S_P	C_P
TiC	-42.337	-3.267	1.835	5.36	6.03	-0.22
TiN	-32.083	-4.473	2.513	4.89	5.03	-0.06
TiO	-45.546	-3.581	2.011	5.35	6.00	-0.14

The requirement of mechanical stability in a crystal leads to the following restrictions on the elastic constants $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. The elastic constants in Table 3 obey these stability conditions, including the fact that C_{12} must be smaller than C_{11}. Our results show that the TM nitrides have a higher bulk modulus than that of corresponding carbide and oxide, and the higher hardness of TiC, TiN and TiO is still explained. As already shown, the study of the bulk modulus is insufficient for a determination of the hardness in TMs and their carbides, nitrides and oxides. Therefore, the elastic constant C can give indications on the hardness of these materials.

We have also reported third order elastic constants and pressure derivatives of $SOEC_s$ are reported in Table 4. Since the present study only emphasizes on two body interaction between the ions particularly in the absence of any experimental data, the refinement of interatomic interaction potential may be made whenever the elastic constants are measured for further insight into the various types of interaction in this group of solids.

Table 5. Calculated experimental values of shear Modulus (G), Young Modulus (E) and Poisson's ratio (σ).

Solids		G (GPa)	E (GPa)	σ
TiC	Prest.	206	479.3	0.16
	Voigt	201[a]	488[a]	0.215[a]
	Reuss	195[a]	477[a]	0.222[a]
	Expt.	203[d]	442.5[b]	-
TiN	Prest.	196	476.1	0.21
	Voigt	216[a]	530[a]	0.229[a]
	Reuss	201[a]	499[a]	0.245[a]
	Expt.	230[c]	475[c]	-
TiO	Prest.	220.5	516.5	0.17

[a] Ref.[24], [b] Ref. [25], [c] Ref. [27], [d] Ref. [20]

The data presented in this paper of shear modulus (G), young modulus (E) and Poisson's ratio (σ) are summarized in Table 5. We know that for a perfectly incompressible material the Poisson's ratio would be exactly 0.5. This allows to draw the conclusion that our materials are not much compressible. In the structural view, the reason for the usual positive Poisson's ratio is that inter-atomic bonds realign with deformation. One more reason is that physically the materials must be stable. Like Ruess calculations of Poisson's, our values more accurately specify that TiN is less compressible or more incompressible than other two TiC and TiO. The theoretically calculated σ of TiC, TiN and TiO are 0.16, 0.21 and 0.17, respectively. The study of the shear modulus G reveals that TiN is hardest in these three materials. Our calculated G values of TiC, TiN (206 GPa, 196 GPa, respectively) matched with the experimental values (203 GPa [27], 230 GPa [20], respectively). The calculated E values of TiC, TiN (479.3 GPa, 476 GPa, respectively) match with experimental values (442.5 GPa [26], 475 GPa [20], respectively). Similarly, we calculated the value of G, E and σ for TiO.

4. Conclusions

The calculated second and third order elastic constants and second order pressure dervivatives demonstrate the predominant ionic nature of the compounds TiC, TiN and TiO. At high pressure these compounds undergo a structural phase transition from NaCl-type structure vto the more dense CsCl-type structure.

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