

# Study of Transition Metal Nitride $Ti_{1-x}Zr_xN$ Alloy at High Pressure

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## Abstract

The structural properties of transition metal nitride using have been explored in the present paper. The study has been extended to  $Ti_{1-x}Zr_xN$  alloy ( $0 \leq x \leq 1$ ) alloy and the effect of composition on structural, and elastic properties are investigated. Phase transition pressure and related volume collapses  $[\Delta V(Pt)/V(0)]$  calculated from this approach are in good agreement with available literature for the parent compounds ( $x=0$  and  $x=1$ ). The present compounds exhibit in rock salt (NaCl) structure at ambient condition, it transforms to cesium chloride (CsCl) structure under high pressure. The results for the mixed crystal counter parts are also in fair agreement with experimental data generated from the application of Vegard's law to data for the parent compounds.

**Keywords,** Alloy, Crystal structure, Phase transitions, High pressure Elastic property.

## 1. Introduction

The transition-metal nitrides have paying substantial attention during the past decades due to their appealing combination of mechanical, electrical, and chemical properties. Transition metal nitrides (TMN) are metallic compounds with outstanding physical properties. They are extremely hard, and their melting temperature is very high. This led to their wide application as hard corrosion resistant coatings and thin films for electronic devices [1,2]. These compounds are stable at high temperatures. These compounds are extremely hard, finding industrial use in cutting tools and wear-resistant parts. Thin films of transition metal nitrides have paid attention for a wide variety of application ranging from tribology to metallization for microelectronics. Transition metal nitrides in the rock-salt (*B1*) structure are widely used for cutting tools and generators due to their high hardness, high melting points, and oxidation resistance [3,4].

Similar to most transition metal nitrides, TiN and ZrN have a NaCl-type structure with space group *FM-3M*. The equilibrium lattice parameter, relative volume  $V=V_0$ , elastic constants  $C_{ij}$ , and bulk modulus of titanium nitride are successfully obtained using the ab initio plane-wave pseudopotential (PW-PP) method within the framework of density functional theory [5]. The elastic properties of ZrN calculated employing all-electron full-potential linearized plane-wave method by Cheng et al. [6]. An investigation on electronic structure, elastic and thermodynamic properties of ZrN under high pressure has been conducted using first-principles calculations based on density functional theory (DFT) with the plane wave basis set as implemented in the CASTEP code by Hao et al. [7]. Lattice dynamics of body-centered cubic-bcc transition metals *B1*-type mononitrides are studied by means of first-principles density functional perturbation theory, ultra soft pseudopotentials, and generalized gradient approximation to the exchange-correlation functional by Isaev et al. [8].

The mixed-metal nitrides of TiN and ZrN have been examined for their melting point and hot hardness behaviour. The intermediate compositions of the ternary system formed are harder than the corresponding binary compounds. The aim of this article is to examine the structural properties of cubic rock-salt  $Ti_{1-x}Zr_xN$  alloy with pressure. Since there are no theoretical studies using the potential model are available for the TMN  $Ti_{1-x}Zr_xN$  alloy. Consequently, we have applied an extended interaction potential model by including zero point energy effects in the Potential model for the prediction of structural properties in  $Ti_{1-x}Zr_xN$  ( $0 \leq x \leq 1$ ) under the effect of pressure. This zero point energy term shows a small effect in Gibbs free energy but to make the model realistic it cannot be ignored completely. The rest of this paper is organized as follows: the model and computational method is given in section 2; the results and conclusion are presented and discussed in section 3.

## 2. Model and computational method

Application of pressure directly results in compression leading to the increased charge transfer (or three body interaction effect [9]) due to the deformation of the overlapping electron shell of the adjacent ions (or non-rigidity of ions) in solids. Also we have considered zero point energy effects, which, is the lowest possible energy that the compound may possess. The energy of the compound is  $(\epsilon = (h\nu)/\{e^{h\nu/kt}-1\} + (h\nu)/2)$ , here  $\nu$ ,  $h$ ,  $t$ , and  $k$  are the frequency, plank constant, temperature and Boltzaman constant of the compound. It is clear from the above expression that even at absolute zero the energy of the compound cannot be zero but at least  $h\nu/2$ . Hence there arises a need to include the zero point energy term in TBP approach for better agreement with experimental approaches.

In the Gibbs free energy ( $G = U + PV - TS$ ) these effects have been incorporated as a function of pressure. Here,  $U$  is the internal energy of the system equivalent to the lattice energy at temperature near zero and  $S$  is the entropy. At temperature  $T=0K$  and pressure ( $P$ ) the Gibbs free energies for rock salt ( $B_1$ , real) and  $CsCl$  ( $B_2$ , hypothetical) structures are given by:

$$G_{B_1}(r) = U_{B_1}(r) + PV_{B_1}(r) \quad (1)$$

$$G_{B_2}(r') = U_{B_2}(r') + PV_{B_2}(r') \quad (2)$$

With  $V_{B_1} (=2.00r^3)$  and  $V_{B_2} (=1.54r'^3)$  as unit cell volumes for  $B_1$  and  $B_2$  phases respectively. The first terms in (1) and (2) are lattice energies for  $B_1$  and  $B_2$  structures and they are expressed as [9]:

$$U_{B_1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{(12\alpha_m z e^2 f(r))}{r} - \left[ \frac{C}{r^6} + \frac{D}{r^8} \right] \\ + 6b\beta_{ij} \exp[(r_i + r_j - r) / \rho] + 6b\beta_{ii} \exp[(2r_i - 1.414r) / \rho] \\ + 6b\beta_{jj} \exp[(2r_j - 1.414r) / \rho] + (0.5)h \langle \omega^2 \rangle_{B_1}^{1/2}$$

$$U_{B_2}(r') = \frac{-\alpha'_m z^2 e^2}{r'} - \frac{(16\alpha'_m z e^2 f(r'))}{r'} - \left[ \frac{C'}{r'^6} + \frac{D'}{r'^8} \right] \\ + 8b\beta_{ij} \exp[(r_i + r_j - r') / \rho] + 3b\beta_{ii} \exp[(2r_i - 1.154r') / \rho] \\ + 3b\beta_{jj} \exp[(2r_j - 1.154r') / \rho] + (0.5)h \langle \omega^2 \rangle_{B_2}^{1/2}$$

With  $\alpha_m$  and  $\alpha'_m$  as the Madelung constants for  $NaCl$  and  $CsCl$  structure respectively.  $C(C')$  and  $D(D')$  are the overall Vander Waal coefficients of  $B_1$  ( $B_2$ ) phases,  $\beta_{ij}$  ( $i, j=1, 2$ ) are the Pauling coefficients.  $Ze$  is the ionic charge and  $b$  ( $\rho$ ) are the hardness (range) parameters,  $r$  ( $r'$ ) are the nearest neighbour separations for  $NaCl$  ( $CsCl$ ) structure  $f(r)$  is the three body force parameter.

The term  $\langle \omega^2 \rangle^{1/2}$  as the mean square frequency related to the Debye temperature ( $\theta_D$ ) as

$$\langle \omega^2 \rangle^{1/2} = k\theta_D/h$$

Here,  $\theta_D$  can be expressed as [12]

$$\theta_D = (h/k) [(5rB_T)/\mu]^{1/2}$$

With  $B_T$  and  $\mu$  as the Bulk modulus and reduced mass of the compounds.

These lattice energies consists of long range Coulomb energy (first term), three body interactions corresponding to the nearest neighbour separation  $r$  ( $r'$ ) (second term), vdW (van der Waal) interaction (third term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second neighbour ions (fourth, fifth and sixth terms), and last term indicates zero point energy effect term.

The mixed crystals, according to the virtual crystal approximation (VCA) [10], are regarded as any array of average ions whose masses, force constants, and effective charges are considered to scale linearly with concentration ( $x$ ). The measured data on lattice constants in alkaline earth oxide mixed  $Ti_{1-x}Zr_xN$  alloy have shown that they vary linearly with the composition ( $x$ ), and hence they follow Vegard's law:

$$a(A_{B_{1-x}}C_x) = (1-x)a(AB) + xa(AC) \quad (5)$$

The values of these model parameters are the same for parent compounds. The values of these parameters for their mixed crystal components have been determined from the application of Vegard's law to the corresponding measured data for  $AC$  and  $BC$ . It is instructive to point that the mixed crystals, according to the virtual crystal

approximation, are regarded as an array of average ions whose masses, force constants and effective charges are considered to scale linearly with concentration. It is convenient to find the three parameters for both binary compounds. Furthermore, we assume that these parameters vary linearly with  $x$  and hence follow Vegard's law:

$$b(A B_{1-x} C_x) = (1-x) b(AB) + x b(AC) \quad (6)$$

$$\rho(A B_{1-x} C_x) = (1-x) \rho(AB) + x \rho(AC) \quad (7)$$

$$f(r)(A B_{1-x} C_x) = (1-x) f(r)(AB) + x f(r)(AC) \quad (8)$$

### 3. Results and discussion

The present potential model contains three model parameters [ $b$ ,  $\rho$ ,  $f(r)$ ]. The values of these model parameters have been computed using the following equilibrium conditions.

$$\left[ \frac{dU}{dr} \right]_{r=r_0} = 0 \quad (9)$$

$$B_1 + B_2 = -1.165 Z_m^2 \quad (10)$$

Where,  $Z_m^2 = Z(Z + 12f(r))$

Using these model parameters and the minimization technique, phase transition pressures of  $Ti_{1-x}Zr_xN$  alloy have been computed for the parent compounds. The lattice constants and bulk modulus have been taken as input parameters of the parent compounds. The input parameters have been taken from our previous paper [11]. The calculated model parameters have been given in Table-1, at different concentrations ( $x$ ).

Table-1 Calculated model parameters of  $Ti_{1-x}Zr_xN$  alloy at different concentration

Alloy/ Concentration	Model parameters		
	$b(10^{-12} \text{ ergs})$	$\rho(\text{\AA})$	$f(r)$
$Ti_{1-x}Zr_xN$ 0	7.9823	0.314	0.001402
0.25	7.0824	0.3122	0.001355
0.5	6.1826	0.3105	0.001309
0.75	5.2827	0.3087	0.001263
1	4.3829	0.307	0.001217

For calculating phase transition we have used the minimization technique. The Gibbs free energies for B1 (NaCl) and B2 (CsCl) phases have been minimized. The phase transition occurs when the change in Gibbs free energies  $\Delta G$  approaches zero ( $\Delta G \rightarrow 0$ ). At phase transition pressure ( $P_t$ ) these compounds undergo a (B1-B2) transition associated with a sudden collapse in volume. The changes in minimized Gibbs free energies of both the phases have been plotted with pressure in Fig. 1.

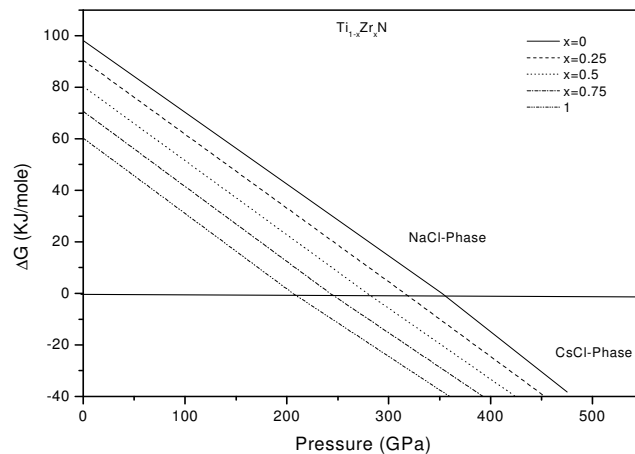


Fig: 1 Variation of  $\Delta G$  (KJ/mole) with pressure for  $Ti_{1-x}Zr_xN$  at different concentrations ( $x$ ).

The plot represents the change in Gibbs free energy at different concentrations ( $x$ ) from 0 to 1. The linear dependency of Gibbs free energy has been seen with concentration ( $x$ ) from this figure. The calculated values of phase transition pressure presented in Table-2 at different concentrations ( $x$ ).

Table-2 Phase transition pressure (GPa) and volume collapse of  $Ti_{1-x}Zr_xN$  alloy at different concentrations

Alloy/ Concentration	Phase Transition Pressure (GPa)		Volume Collapse (%)
	Present	Others	Present
$Ti_{1-x}Zr_xN$ 0.0	352.0	354 <sup>a</sup>	4.0
0.25	315.5	317.75 <sup>a*</sup>	4.25
0.5	279.0	281.5 <sup>a*</sup>	4.50
0.75	242.5	245.25 <sup>a*</sup>	4.75
1.0	206	209 <sup>a</sup>	5.0

a-ref [12]

a\* pseudo-theoretical values [interpolated from the others experimental values of the two end crystals

The variation of phase transition pressure with concentration has been plotted in Fig. 2.

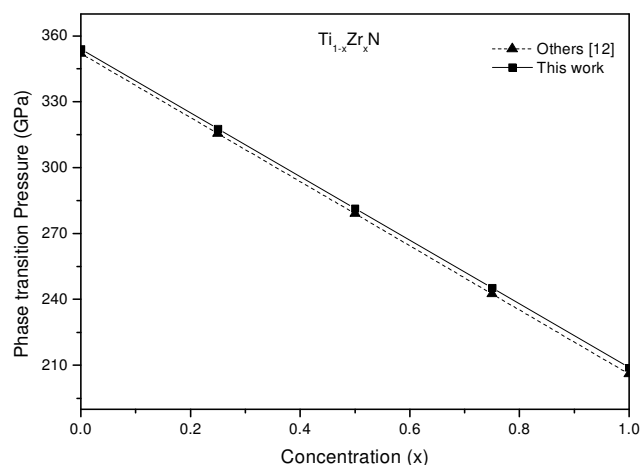


Fig: 2 Variation of phase transition pressure with concentration ( $x$ ). Solid squares represent

The values for different concentrations ( $x$ ) have been compared with pseudo-theoretical (interpolated from the theoretical values of the two parent crystals) calculations [12].

These plots represent linear dependency with concentration ( $x$ ). The relative volume changes  $V(P)/V(0)$  corresponding to the values of  $r$  and  $r'$  at different pressures have been calculated. The values of relative volume changes  $V(P)/V(0)$  have been plotted with different concentrations ( $x$ ) in Fig. 3.

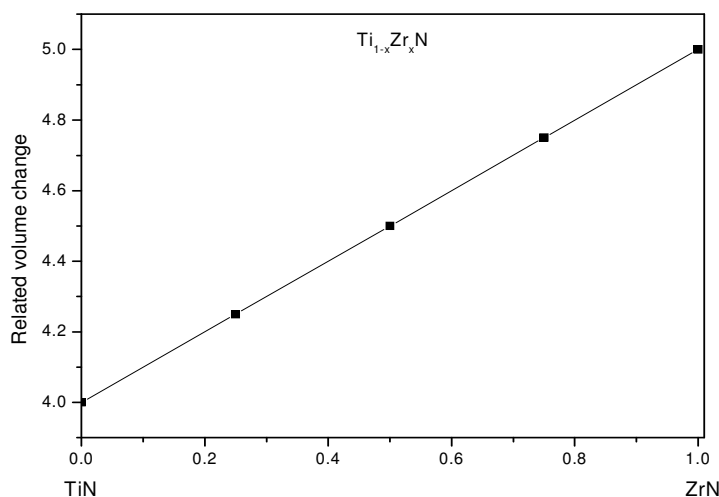


Fig: 3 Variation of volume change (%) with concentrations ( $x$ ).

## 5. Conclusion

The extended interaction potential EIP model has been applied to investigate the structural phase transition and volume collapse of transition metal nitride alloy  $Ti_{1-x}Zr_xN$  ( $0 \leq x \leq 1$ ) under high pressure. Phase transition pressures and associated volume collapses calculated from present approach are in good agreement with available results for the parent compound ( $x=0$  and  $x=1$ ). The results of present alloy also show the same trend as reported with pseudo-theoretical calculations generated from the application of Vegard's law to data for the parent alloy. Finally, it may be concluded that in general, our values are near to available theoretical data for the parent compounds and pseudo-theoretical data for mixed concentration. The successful predictions achieved from the present model considered overlap repulsion interaction effective up to second neighbour ions and including the zero point energy effect

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