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# Phase Transition in Mixed Transition Metal Oxides under High Pressure

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**ABSTRACT:** *Mixed crystals can be categorized as the crystal in which two or more different types of atoms are present and configured. These atoms interact each other in the influence of Coulomb force of attraction and the presence of short range repulsion force. Due to this interaction they tends to be arranged in equilibrium state and forms new material. A pure crystal can be doped by impurities with proper concentration of impurity to get the desired material. This concept of interaction between the atoms are called the Three Body Interaction(TBI) model. This model is based on the concept of interaction between atoms. The presence of short range repulsion force between the atoms is very crucial, in the absence of which coulomb force of attraction will be dominant and it will lead to volume collapse. Applying of high pressure on the crystal results in the transfer of charge between the atoms. This transfer of charge causes them to rearrange in some different cofigurational state different from original configuration. This rearrangement of atoms affects the different properties of material like hardness, melting point, optical properties and mechanical properties.*

## I. Introduction

Material is always very important for human being. It has very significant role in the development of Economy as well as technological development of country and society. Over a long period of time material has been used in different form by our civilization. In lieu of this, recently very advanced techniques has been developed to study the phenomena of Phase Transition in materials. This increases our interest to study the behavior of material under very high pressure. We will now focus on the study of phase transition in mixed crystal. Considerable efforts have been made to understand the dynamic and static behavior of mixed crystal but it is not enough to understand their phase transition and different properties. In the mixed crystal the arrangement of atoms are somewhat different from pure crystal as well as from impure crystal. This arrangement and concentration of atoms in mixed crystal determines the properties of the solid. By the doping of impurities the arrangement and concentration of atoms can be manipulate to get the crystal of desired properties. Development of new material by doing this is very significant and can be applied vastly in industries. This is also of great technological and academic interest. In our present work we will try to focus on the behavior and properties of mixed crystals. It is therefore the study of static properties, cohesion energy and phase transition phenomena of mixed crystal is very significant and important. It helps us to understand the nature of interionic forces in mixed solid crystals under very high pressure. A large number of efforts have been made to study the nature of interionic forces in mixed crystal. The techniques used for above purpose are measurements of elastic constants[1-6], phonon dispersion curves[3-14], Raman and infrared absorption [15-19] and phase transition studies[20-21].

## II. Theory

On the basis of several studies, various properties of mixed ionic crystals can be derived successfully. It is based on the assumption that their variation from one member to another is linear. These details have been reviewed by phonon dispersion curves from neutron scattering techniques [3-6]. An interionic potential model for the study of lattice static and dynamic properties of mixed crystal in the virtual crystal approximation[25] was developed by Singh and co-workers [22,23]. Accordingly it is also assumed that mixing of atoms are distributed randomly and are in proportion to molar concentration of substituting ions [23]. This interionic potential model consists of long - range coulomb interaction and three body interaction [ arising form charge transfer effects(1)]. This potential model has successfully predicted the phase transition pressure and associated volume collapses of mixed crystals. As we are aware that mixing or alloying of different compounds results into the improvement of its mechanical properties such as hardness etc. Most of the Transition Metal Compounds which are available presently shows high hardness and high melting points. Hardness is the most significant parameter in the study of mixed compounds which increases the importance of the study of mixed transition metal compounds. Jhi et al [26] considered the mixed system of TiC and TiN for the study and found that their hardness improves considerably with 50% nitrogen concentration. They have also included the analysis of cohesive properties and bulk modulus of $TiC_xN_{1-x}$n mixed system and found that the calculated equilibrium

volume of the $TiC_xN_{1-x}$alloy obeys the Vegard's law [ Veq(x) = xVeqTic+(1-x)VeqTiN]. After the study it has been found that the mixed system of $TiC_xN_{1-x}$ is stable in complete range of carbon concentration and its bulk modulus increases with the increase in concentration of Nitrogen.

In the mixed crystals spatial arrangement depends on the molar concentration of impurity in the host solid without disturbing its lattice topology. After the X-ray analysis it is found that mixed ionic crystals are the mixture of pure components and they are truly crystalline. Whenever there is change in concentration from one pure member to another, their lattice constant also changes linearly. Thus unlike glasses any disorder in mixed crystal is configurational. The mixed crystal can also be classified as the intermediate between the perfect and disordered solids. Mostly the properties of the mixed crystals varies linearly with the variation of their components, which is verified by the measurement of unique lattice constants in all types of mixed crystals. The effect of three body interaction(TBI) concept in a mixed crystal is also very significant. This is because due to presence of doped atom $B^-$ in system. These TBI therefore are expected to play an important role in most of the properties between the ions of $B^-$ and $C^-$. The interionic potential model for mixed crystal under consideration is based on the assumption that the lattice $Ab_xC_{1-x}$ system is composed of pseudo unit cells [24]. In this sites corresponding to one sub lattice is occupied by atom A and other sub lattice is occupied by both [=(1-x)B and C=[xC] atoms. By this way the periodicity of lattice is maintained.

To describe the interaction between different ions in the mixed crystal, we have assumed the following points [22,23].

1. The symmetry of the mixed crystal system remains the same as that of host crystal.
2. The change in force constants is small.
3. The short range interactions are effective up to second- neighbor ions.
4. The atoms are hold together with harmonic elastic forces without any internal strains within the crystal.

These assumptions are consistent with the virtual approximation of mixed crystal [25]. From the experimental investigations [24,27] it is clear that such approximations can explain the elastic and phonon properties of mixed crystals property. The interaction potential of host and mixed crystal corresponding to an interionic separation $r_{ij}$ can be written as follows:

"(1)" $U(r) = -\Sigma Z_iZ_je^r r_{ij}^{-1} + \Sigma Z_iZ_je^2 r_{ij}^{-1} fm(r) + \Sigma c_{ij} r_{ij}^{-6} + \Sigma d_{ij} r_{ij}^{-1} + \Sigma b \beta_{ij} \exp[(r_i+r_j-r_{ij})/\rho]$

In the above equation the first term is coulomb energy. Second term represents the three body interaction which arises from the charge transfer effect[1] between the adjacent ions. The TBI parameter fm(r ) is dependent on the overlap integrals [28,29] and its functions from of mixed crystal can be written as follows:

"(2)" $f_m(r) = (1-x) f_1(x) + x_2f_2(x) + (1-x) f_1(x) + f_2(r)^{½}$

Where the function $f_\alpha$ ($\alpha = 1,2$) corresponds to the two types of crystals and denoted by

"(3)" $f\alpha(r) = f_0 \exp(-r_\alpha/\rho_\alpha)$

The third and fourth term in eq. (1) represents the vanderwall energy (vdW) with $C_{ij}$ and $d_{ij}$ as vdW coefficient due to dipole-dipole(d-d) and dipole-quadrupole (d-q) interactions. These coefficients are calculated from the SKV method[30]. For the mixed crystals their linear variation can be expressed as follows.

"(4)" $C_{ij}^m = (1-x)C_{ij}^{(1)} + x C_{ij}^{(2)}$

"(5)" $d_{ij}^m = (1-x)d_{ij}^{(1)} + xd_{ij}^{(2)}$

According to the framework of Hafemeister and Flygare (HF) potential [31] the last term in Eq. (1) is the short range overlap energy, Here Bij are the pauling coefficients, P is the probability of interaction between different type of atoms, $b_\alpha$ and $\rho_\alpha$ are the short range parameters, $r_i$ and $r_j$ represemts the ionic separation between two interacting ions i and j. From the equation (1) we can say that our present interionic potential model depends on only three parameters b, ρ and fm(r ) for the host crystals. These parameters are determined from the equilibrium condition and elastic constants. However for mixed crystals the parameters can be derived from host solids followed by Vegard' law.

The interionic potential model discussed above can also be applied to derive the harmonic and anharmonic elastic constants, which can be derived from second- order derivative of potential energy given by Eq (1)

with the help of homogeneous deformation [31]. We have studied the elastic behavior of mixed crystals $TiC_xN_{1-x}$ , $TiO_xN_{1-x}$ and $TiC_xO_{1-x}$ which are important in technological development and fast ionic conduction. These crystals crystallizes in NaCl and CsCl structures.

## III. Results And Discussion

We have studied the properties of intermetallic compounds $TiC_xN_{1-x}$ , $TiO_xN_{1-x}$ and $TiC_xO_{1-x}$ using our present model. The compounds are considered to be in the NaCl phase, in which transition metal atoms M substituted by N atoms in the present structure [26]. The optimized lattice constants are shown to be in good agreement with the corresponding experimental data. When M component changes form C to N, it decreases the

volume of $TiC_xN_{1-x.}$ The ferromagnetic state for the compound is more energetically favorable for the compound with M=Ti, while in case of CsCl the structure is found to be antiferromagnetic. In these compounds it is the M atom which causes to originate the magnetism. The ferromagnetic coupling is mediated through the indirect d-d and d-q exchange interactions. The transport calculation based on spin shows that spin polarization in diffusive region is significantly higher than that in the ballastic one for these intermetallic compounds.

Jhi [26] has measured the electronic structure and structural stability of $TiC_xN_{1-x}$ alloys, but probably not much theoretical work has been done on $TiC_xN_{1-x}$ alloy. We have studied and investigated the structural stability and elastic stiffness of $TiC_xN_{1-x}$ , $TiO_xN_{1-x}$ and $TiC_xN_{x-1}$ alloy using three body potential model (TBPM).On the basis of calculation it can be stated that the alloy is stable in the complete range of the carbon and oxygen concentration. The three body potential model (TBPM) has also been applied to evaluate the pressure derivatives of the second order elastic constants of $TiC_xN_{1-x}$ and a good agreement with the experimental values has been obtained. The present approach is suitable for the description of elastic constants and associated properties of Transition Metal Compounds.

Further the variation of the second and third order elastic constants with pressure have followed a systematic trend which are almost identical to those exhibited by the alkyl halides having NaCl (B1) structures. Third Order Elastic Constants (TOEC) for mixed crystal system are in good agreement with the available theoretical results. The variation of TOEC for the intermediate compounds having different concentration shows a linear decrease in values with the increase in pressure. These trends are similar to the trends suggested by Vegard's law [Veq(x) = xVeqTic+(1-x)VeqTiN ].

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