Phase Transition in Titanium Oxide under High Pressure

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Abstract *:Transition metal oxides are very interesting, useful and technically relevant materials due to their nature of existence. We have studied the nature of TiO as transition metal oxide and their phase transition under high pressure. We have explored the effect of high pressure on transition metal oxides with the help of proper potential model. A theoretical study of phase transition under high pressure and elastic behavior of transition metal oxides using three body interaction potential model is the result of deformation of electron shells due to overlapping of ions. Transition metal oxides are very hard in nature that is why phase transition occurs at very high pressure. We have applied three body potential model to study transition in Titanium Oxide(TiO). TiO exhibits phase transition from relatively less densed NaCl structure to more densed CsCl atomic arrangement. Under very high pressure TiO undergoes phase transition from B1(Rocksalt) to B2(CsCl). Structure which is associated with a sudden collapse in volume shows first order phase transition.*

I.   Introduction

Transition metal oxides is one of most interesting class of solids which shows different variety of novel properties [1-5]. These properties arises due to the outer *'d'* electron present in the ions of transition metals. These outer *'d'* electrons can not be detected by neighboring atoms. The intermediate character of these electrons exhibits itself in terms of behavior of localized electrons in some oxides. In some oxides they shows collective behavior also. Both kinds of *'d'* electrons can also exists at the same time at some instances. During last few years the field of transition metal oxides have become very intensive and of great interest for condensed matter physicist because of its vast properties. The nature of bodings in these oxides varies from ionic to covalent. In the TiO metallic bonding has been found. As far as the crystal structure is concerned, in the case of transition metal oxides it varies from cubic to triclinic symmetry. The composition of TiO, which is binary composition of oxides possess the rock-salt structure. When phase transition occurs in these oxides their structure changes from one type to another. For example under high pressure the structure of TiO get changes from the structure of NaCl to the structure of CsCl. Another interesting thing associated with this phase transition is the change in the magnetic, electrical, thermodynamical and optical properties of these crystals. Some oxides including TiO shows a wide range of non-stoichiometry. These deviations in stoichiometry occurres due to the deficiency of cation or anion. If this deviation in stoichiometry is very large it causes to change in the structure of crystal. Transition metal oxides shows a wide range of electrical conductivity which is affected by deviations for stoichiometry.

This oxides exhibits a wide range of magnetic properties also. The properties of transition metal oxides can also be changed through adding impurities or by doping intentionally .The study of high pressure on different material are very important in the development of the basic science as well as from applied point of view. Transition metal oxides has very vast application in Scientific, Research and Industrial technologies.[6-9]. In the present investigation we have focus on phase transition of Titanium Oxides under very high pressure. The transition metal oxides MO(M-Metal Element, O-Non-metallic Element) are very hard, wear and corrosion resistance and having high melting point.[6-8]. TiO can replace Tungesten Carbides for a cutting tool material.
A first order phase transition is characterized by the discontinuity in volume which is given by the first order derivation of Gibbs Free Energy. If the different variables like, temperature, pressure, electric field, magnetic field acting on a system is varied, the free energy of the system also changes. If such changes or variations in the free energy are associated with the atomic or electronic arrangement or configuration of the system, we can say that phase transition is occurring.[14]

The three body interaction arises from the transfer of charge during overlapping of ions. This is incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure (P) and three body interaction (TBI). The value of interionic separation is calculated by minimizing the Gibbs free energy at different values of pressure. Phase transition pressure is computed at the pressure where difference in Gibbs free energy becomes zero.We will provide adequate and realistic information about various types of interionic interaction in the our present work. These are long range Coulomb interaction, three body interaction and overlap repulsion working between first and second neighbour ions in the ionic crystals of the NaCl(Rocksalt) structure. The three body

potential model is very effective as far as description of phonon transition, phonon dispersion, harmonic and unharmonic properties of ionic and semiconductor solids are concerned. One more good feature of the present theoretical work is that it requires minimum number of parameters for calculation. We can calculate different properties to explore the behavior of matter under very high pressure. These properties are behavior of matter under high pressure, phase transition pressure, second order elastic constants, behavior of second order elastic constant under high pressure and volume collapse. In this model only three parameters [b, ρ and f(r)] are used, where b is the hardness parameter, ρ is range parameter and f(r) is the three body parameter. The three body parameter f(r) is calculated from the cohesive energy and its first order derivates. Three body parameter can be expressed as f(r) = fo exp(-r/ ρ).

II.   Theory and Method

When pressure is applied to a crystal it results into the transfer of charge between the atoms which can also be stated as three body interaction [11]. Due to this pressure ions gets overlapped with each other and this causes in the deformation of electron shells. A particular lattice structure can be said in stable state when the value of Gibbs free energy $(G = U + PV – TS)$ is at its minimum level. Where U is the internal energy which is equal to lattice energy at 0^0 K and S is the vibrational energy at absolute temperature T. The application of high pressure on a crystal leads to compression or decrease in volume which cause in the increase of charge transfer due to three body interaction. Three body interaction are of significant importance at very high pressure where interionic separation reduces remarkably and co-ordination number increases.

The Gibbs free energy, at T = 0^0 K and pressure (P), for the real (B_1) and hypothetical (B_2) phases is given by

$$G_{B1}(r) = U_{B1}(r) + PV_{B1} (=2.0r^3) \text{ -----------------------------(1)}$$

$$G_{B2}(r) = U_{B2}(r) + PV_{B2} (=1.54r^3) \text{ -----------------------------(2)}$$

Where the first term in the above equations represent the lattice energies for the B_1 and B_2 structures expressed as

$$U_{B1}(r) = -\alpha_M Ze^2 (Z + 12f(r)/r + 6b\beta_+ \exp(r_+ + r_- -r')/\rho)$$
$$+ 6b\beta_+ \exp(2r_+ - 2r)/\rho) + 6b\beta_- \exp(2r_- - 2r)/\rho) \text{ --------------(3)}$$

$$U_{B2}(r') = -\alpha_M Ze^2 (Z + 16f(r)/r + 8b\beta_+ \exp(r_+ + r_- -r')/\rho)$$
$$+ 3b\beta_+ \exp(2r_+ - 2r)/\rho) + 3b\beta_- \exp(2r_- - 2r)/\rho) \text{ --------------(4)}$$

Here, the first two terms are the long range Coulomb and TBI energies [13]. The remaining terms corresponds to the overlap repulsion represented by Hafemeister and Flygare (HF) potential and extended upto the first (+ -) and second (+ + and - -) neighbour ions, α_M (α'_M) is the Madelung constant for B_1 and B_2 phase β_{ij} (ij= + -) are the Pauling coefficients. Ze is the ionic charge with e as the electronic charge b(ρ) are the range (hardness) parameters, r+(r) is the ionic radii of +(-) ions taken from Ref.,r(r') is the nearest neighbour separation of $B_1(B_2)$ phase and they may be conveniently expressed as $f(r) = f_0 \exp(-r/\rho)$ [7] with f_0 as a constant. The lattice energies given by the eqs (3) and (4) contain only three model parameter (b, ρ and f(r)). Hardness is very important issue in the study of titanium oxides. It involves the plastic deformation of materials which depends critically on the motion of dislocations. In the present scenario theoretical calculations can be useful in establishing in search of improved materials properties which can be helpful for experiments. In the case of NaCl calculation demonstrate that structure studies are very useful in experiments

III.   Results and Discussion.

After studying the different values of interionic separation at different pressure using the minimization technique we found that at the phase transition pressure, the difference between Gibbs free energy becomes zero. Phase transition pressure of TiO shows that our model has correctly predicted the relative stability of structure. In the phase transition from B1 to B2 structure, the inter-ionic separation reduces and coordination number increases. In view of above discussion we may hope that the findings of this paper will certainly stimulate the work on the TiO. Finally we may concludes that the present three body potential approach is fairly adequate for the study of high pressure phase transition, volume collapse, bulk modulus and second order elastic constants..

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