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RESEARCH ARTICLE

COHESIVE ENERGY OF ZnO DOPED WITH TRANSITION METAL IONS UNDER PRESSURE.

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Abstract

In the present paper, we have investigated the cohesive energy of ZnO with transition metal ions (ZnO:TM, TM= Mn, Co and Ni) at ambient pressure and at phase transition pressure. Here we have used three-body potential model (TBPM) to study ZnO:TM find that the cohesive energy at doping concentrations in zinc blende and rock salt (B_3+B_1) structures and cohesive energy increases of ZnO:TM with increases doping concentrations of transition metal. When pressure raised from an ambient condition, ZnO:TM transforms from B_3+B_1 to B_1 structure at phase transition pressure. Phase transition pressure and cohesive energy of ZnO:TM always decreases with increases doping concentration of transition metal (Mn, Co, or Ni), but the phase transition path is not affected by doping and accelerates the phase transition pressure.

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Introduction:-

Zinc oxide (ZnO) is a typical II–VI semiconductor with a wide band gap ($E_g = 3.36$ eV) and a large exciton binding energy (60 meV). It has various practical applications including solar cells [A.B.F. Martinson et al 2009], optoelectronic devices [H. Kim et al 2000], catalysts [M.H. Sarvari et al 2005], chemical sensors, field-effect transistors [J.J. Schneider et al 2008], piezoelectric transducers, etc. Several different crystal structures of ZnO including rock salt (B_1), CsCl structure type (B_2), zinc-blend (B_3) and wurtzite (B_4) have been reported [S.E. Boulfelfel et al 2008 and S. Desgreniers 1998] under different thermodynamic conditions. The thermodynamically stable phase of ZnO at ambient condition is B_4 hexagonal structure which is fourfold-coordinated and B_3 structure is another fourfold-coordinated structure which can be stabilized by the epitaxial growth of ZnO on cubic substrates and transforms into a cubic rock salt (B_1) phase under high pressures. A number of experiments indicated that at room temperature the phase transition occurs at about 9 GPa with a volume decrease of 17% [S. Desgreniers 1998, J. M. Recio et al 1998, H. Karzel et al 1996]. Bates, White, and Roy [C. H. Bates et al 1962] reported phase transition in the range of 10 GPa. Recently, it has been well-established that the pressure at which the phase transition takes place is around 8.7–10.0 GPa with a volume change ($\Delta V/V$) of 16.7–18.13% [Chih-Ming Lin et al 2014]. Y. Mori et al [Y. Mori et al 2007] investigated for Mn-doped ZnO and Co doped ZnO by high-pressure X-ray powder diffraction technique using synchrotron radiation. MnO, CoO and NiO have rock salt (B_1) structure at ambient pressure. Doping is an efficient approach to improve the structural properties of materials. In the present research work we have developed a three body potential model (TBPM) to study the cohesive properties of ZnO doped with transition metal (TM) ions (Mn, Co or Ni) at ambient pressure and at phase transition pressure.

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Methods:-

Under normal condition, solids exhibit a particular crystal structure, for which the cohesive energy and Gibbs free energy is minimum, but under the high pressure and /or temperature condition the atoms rearrange themselves and assume a new stable structure again for which the cohesive energy as well as Gibbs free energy of the solid is minimum. However, on application of high pressure the atomic arrangement in solid change resulting into change in interatomic distance, crystal structure and relative volume change, it has been found to show sudden discontinuity corresponding to the volume collapse, which occur during the phase transition as the system goes from rarer to denser crystal structures. The pressure at which such structure change occurs is called phase transition pressure. The Gibbs free energy of a system is given by

$$G = \phi + PV - TS$$

In case of pressure induced phase transition in crystals, when phase transition occurs from first phase to second phase, at $T=0K$ and transition pressure P , at phase transition pressure P_t , $G(B_3) = G(B_1)$ (for B_3 to B_1 transformation). Here the abbreviation ϕ represent cohesive energies of crystal.

$$\phi(r) = -\sum_{ij} \frac{z_i z_j e^2}{r_{ij}} \left(1 + \frac{2n}{z} f(r_{ij}) \right) - \sum_{ij} \left(\frac{c_{ij}}{r_{ij}^6} \right) - \sum_{ij} \left(\frac{d_{ij}}{r_{ij}^8} \right) + nb\beta_{\pm} \exp\left(\frac{r_+ + r_- - r}{\rho}\right) + \frac{n'}{2} b\beta_{++} \exp\left(\frac{2r_+ + k_1 r}{\rho}\right) + \frac{n'}{2} b\beta_{--} \exp\left(\frac{2r_- + k_2 r}{\rho}\right)$$

The first and second term in it are the long range coulomb and three body interaction, the third and fourth are short range van der waals attraction and the remaining terms represent the short range overlap repulsion operative up to the second neighbour ions.

Result and Discussion:-

In the present work, we have investigated the cohesive energy at ambient pressure and phase transition when two pure binary materials having different structure are mixed. These two pure binary materials are the ZnO with a zinc-blend (B_3) structure and the TMO (TM=Mn, Co, Ni) with a rock salt (B_1) structure at ambient pressure. We have computed the cohesive energy of ZnO:TM at different doping concentrations. Cohesive energy is found to increase with doping concentration for all the three ZnO:TM (Mn, Co, Ni) mixed crystals as shown in figure (1). When the pressure is raised from an ambient condition, ZnO transforms from B_3 to B_1 structure. In the present investigation, we have used TBPM to study the pressure induced structural phase transition in ZnO:TM (Mn, Co, Ni). We find that the phase transition pressure of ZnO, when doped with different types of transition metal ions (Mn, Co, Ni) is always founds to decrease with increasing doping concentrations, but the phase transition path is not affected by the doping and accelerates the phase transition pressure shown in figure (2). With the knowledge of cohesive energies of present crystals, we have predicted the relative stability of the competitive structure B_3 and B_1 . We have evaluated phase transition from graphical analysis in which the Gibbs free energy difference $\Delta G = G_2 - G_1$ corresponding to the above cohesive energies have been computed for $Zn_x Mn_{1-x} O$, $Zn_x Co_{1-x} O$, and $Zn_x Ni_{1-x} O$ at different doping concentration (x). The pressure at which ΔG approaches zero corresponds to phase transition pressure (P_t). The variation in cohesive energy of ZnO:TM with doping concentration at phase transition pressure have been plotted in figures (3). It is evident that this variation is almost linear.

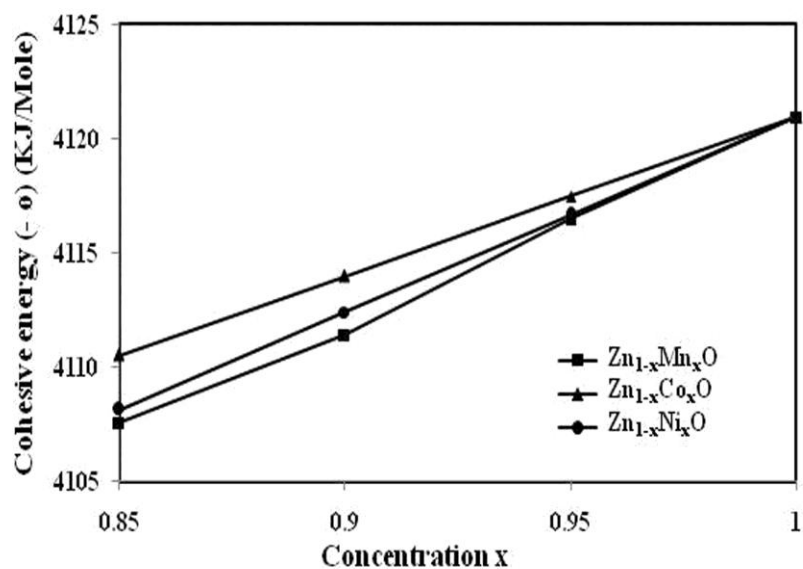


Fig. 1:- Cohesive Energy V/s Concentrations at ambient pressure ZnO:TM.

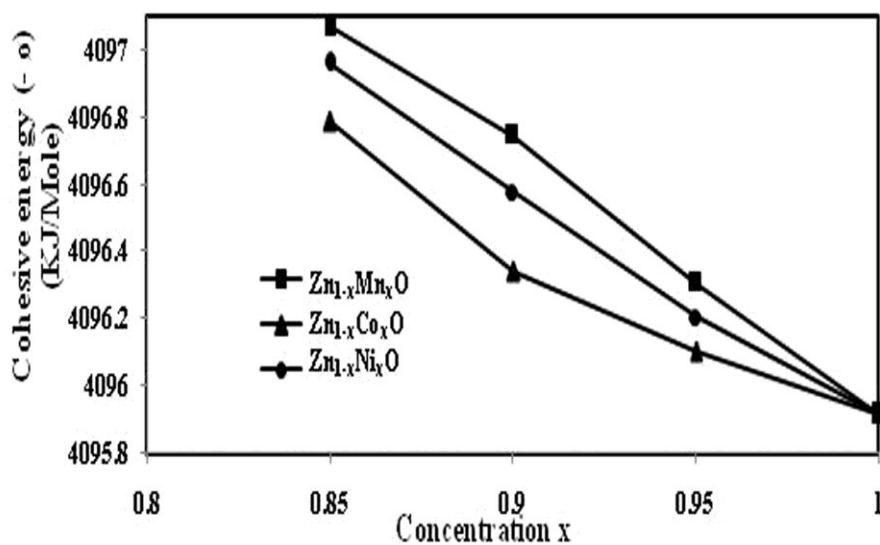


Fig. 2:- Cohesive Energy v/s Concentrations at phase transition pressure ZnO:TM.

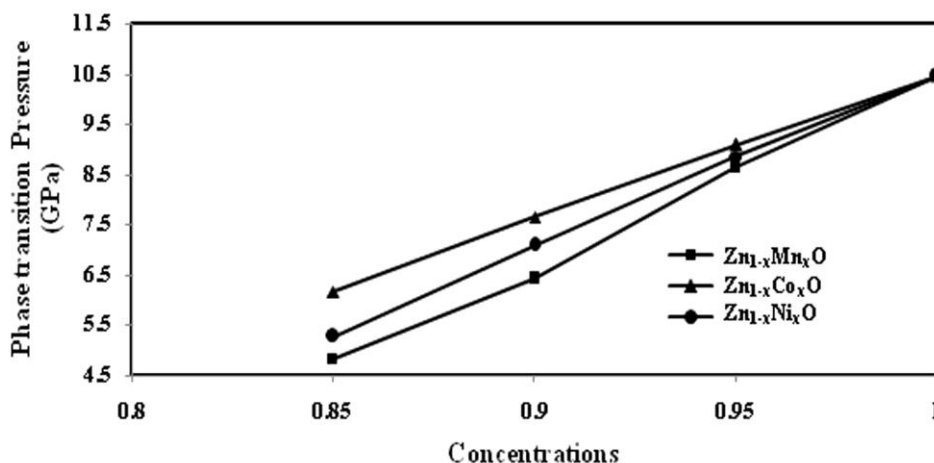


Fig. 3:- Phase transition Pressure V/s Concentrations ZnO:TM.

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