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**RESEARCH ARTICLE**

# Structural properties of $CdS_{1-x}Se_x$ mixed crystal under high pressure

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## *Abstract*

The present work is intended to investigated structural properties $CdS_{1-x}Se_x$ under high pressure have been evaluated using three body potential model (TBPM) at six different concentrations x(x=0, 0.2, 0.4, 0.6, 0.8, 1). This potential has only three model parameters. The experimental data have been generated for $CdS_{1-x}Se_x$ by the application of Vegard's law to experimental values available for pure end-point members (CdS and CdSe). The Structure of $CdS_{1-x}Se_x$ have been Zinc-blend (B3) at ambient pressure and with increasing pressure, they undergo zinc-blend ($B_3$) to Rock salt ($B_1$) phase transition. Predicted phase transition pressures have been good agreement with experimental and other theoretical data. The variation of Phase Transition Pressure and Lattice constants have almost been linear with concentrations. Structural properties intermediate between those of the end-point members.



## Introduction

Over the past few years, study of materials under high pressure has become an extremely important subject displaying explosive growth, Looking to many fold advantage of alloy, several workers have investigated them both theoretically and experimentally. For X-ray structure analysis it has been observed that the mixed ionic crystal are formed by the mixing of pure components and are truly crystalline and their lattice constants change linearly with concentration from one pure member to another (Purvee, Bhardwaj et al 2008). According to virtual crystal, approximation (VCA)(R J Elliot and R A Leath 1976) the mixed crystals are regarded as average ions whose masses, force constants and effective charges are considered to scale linearly with concentration (x). Alloys represent important classes of materials ranging, their mechanical, electrical and magnetic properties can be controlled by composition of another material mixed in a pure material. Cadmium chalcogenides and their alloy have attracted special attention in recent years for their properties such as Structural (S. Wei, S.B. Zhang 2000, N. Benkhettou et al 2004), electronic (M. Cote et al, 1997, O. Zakharov et al 1994), thermodynamic (A. Tomasulo et al 1996, M.B. Kanoun et al 2000, A. Mujica et al 2003), and optical properties(A.E. Merada et al 2005). These chalcogenides have wide range of applications such as γ-ray detectors, infrared windows, solar cells and other optoelectronic devices (S. Wei, S.B. Zhang 2000 ) etc.. Recently $CdS_{1-x}Se_x$, (Cadmium-sulfur-selenium) becomes an area of great technological activity because of this has the possibility to produce novel material such as blue-green laser diode based on these compounds(S. Ouendadji et al 2010) and $CdS_{1-x}Se_x$ color glasses are usually synthesized in two steps(Ekimov A 1996). The phase dynamics of the electronic states of $CdS_{1-x}Se_x$ investigated under various experimental conditions. At low temperature, it showed that the screening of the Coulomb interaction reduces the scattering rates between electrons (J. C. Merle et al 1996)[12]. Urte Hotje et al investigated crystallographic parameters of ZnS, ZnSe, CdS, CdSe and thier Mixed Crystals have been determined by X-ray powder methods (Urte Hotje et al 2003)and S. Quendadji et al studied the structural, electronic, optical and thermodynamic properties of $CdS_{1-x}Se_x$ and $CdS_{1-x}Te_x$ semiconductor alloys using generalized gradient approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) and Engel–Vosko (EV) (S. Ouendadji et al 2010). E. S. Freitas Neto et al investigated Resonant Raman scattering in $CdS_{1-x}Se_x$ nanocrystals (E. S. Freitas Neto et al 2010)

.V.P. Kunets et al investigated the optical properties of thermo-stimulated changes in an ensemble of $CdS_{1-x}Se_x$ quantum dots embedded into borosilicate glass matrix(V. P. Kunets et al 2001).
Structure of CdS and CdSe has been Zinc-blend ($B_3$) at ambient pressure and with increasing pressure; they undergo Zinc-blend ($B_3$) to rock salt ($B_1$) structure phase transition at 2.5GPa and 3GPa respectively. Similarly, their mixed compounds $CdS_{1-x}Se_x$ ($0\leq x\leq 1$) also under goes Zinc blende to Rock Salt ($B_3\rightarrow B_1$) phase transition under high pressure. The difference between phase transition pressures of end-point members is very low only 0.5GPa. In the present study the structural properties for $CdS_{1-x}Se_x$ ($0\leq x\leq 1$) with respect to different concentration(x) (x=0, 0.2, 0.4, 0.6, 0.8, 1) under high pressure have been evaluated using by TBPM and input parameters generated by using Vegard's law. The phase transition pressures have been evaluated by graphical analysis, which the Gibbs free energy difference is plotted against to the pressure for different concentration x and we are plotted phase diagram at different concentrations. Predicted Phase transition pressure, lattice constant and volume collapse are good agreement with available experimental and other theoretical model.

## Methodology

In the proposed work, a suitable three body potential approach under the framework of rigid ion model have been developed to investigate the pressure induced phase transition of mixed crystal $CdS_{1-x}Se_x$($0\leq x\leq 1$) The input data is evaluated with the help of Vegard's law.

The interatomic potential(P. O. Lowdin 1956, S. O. Lundqvist 1957, R. K. Singh 1982, R.K. Singh and M.P. Verma 1970,1971, F.G. Fumi anf M.P.Tosi 1962, J.C. Slater and J.G. Kirkwood 1931) of the compounds in the framework of the rigid ion model expressed as

$$\emptyset = \emptyset_c + \emptyset_T + \emptyset_R \qquad (1)$$

$$\emptyset = \sum_{ij} \frac{Z_i Z_j e^2}{r_{ij}}\left(1+\frac{2n}{Z}f(r_{ij})\right) + b\left[n\beta_{+-}\exp\left(\frac{r_+ + r_- + r_0}{\rho}\right) + \frac{n'}{2}\left\{\exp\left(\frac{2r_1 + kr_0}{\rho}\right) + \exp\left(\frac{2r + kr_0}{\rho}\right)\right\}\right] \qquad (2)$$

The first and second term in it are the long-range Coulomb and three body interaction and the remaining terms represent the short range overlap repulsion operative up to the second neighbor ions. Here b and ρ are hardness and range (Strength) parameters and can be determined from the Equilibrium condition.

Thermodynamically, a phase transition is said to occur when change in the structural detail of the phase are caused by a variation of the free energy. The stability of a particular structure has decided by the minimizing of the Gibb's energy, which is given as (where U is internal energy) G=U+PV-TS ; But at 0K temperature; G=U+PV

For predicting transition pressure we will minimizes the Gibb's free energy with respect to inter ionic separations and calculate $\Delta G=G_1(r) - G_2(r)$ for various pressure. The Gibb's free energies $G_1(r)$ for one phase and $G_2(r)$ for second phase become equal at the phase transition pressure P .i.e. $\Delta G=G_1(r) - G_2(r)$ become zero.

Vegard's law(L. Vegard et al 1921, Harvard edu A. R. Denton et al 1991) is an approximate empirical rule, which holds that a linear relation exists, at constant temperature, between the crystal lattice parameter of an alloy and the concentrations of the constituent elements. The expression for vegard's Law is

$$a(AB_{1-x}C_x) = (1-x)a(AB) + xa(AC) \qquad (3)$$

where
$AB_{1-x}C_x$= $CdS_{1-x}Se_x$, AB=CdS and AC=CdSe
Input parameter b, ρ and f(r) can be determined by using vegard's Law

$$b(AB_{1-x}C_x) = (1-x)b(AB) + xb(AC) \qquad (4)$$
$$f(r)(AB_{1-x}C_x) = (1-x)f(r)(AB) + xf(r)(AC) \qquad (5)$$
$$\rho(AB_{1-x}C_x) = (1-x)\rho(AB) + x\rho(AC) \qquad (6)$$

## Result and Discussion

The present result obtained using the present theoretical model. The values of input data at different concentration x (x=0, 0.2, 0.4, 0.6, 0.8, 1) have been determined by equilibrium condition and Vegard's law, that values listed in Table (A). Using values of these model parameters calculated cohesive energy for $CdS_{1-x}Se_x$ having Zinc blende structure. We have evaluated phase transition from graphical analysis in which the Gibb's free energy difference $\Delta G=G(B3)-G(B1)$ corresponding to the above cohesive energies have been computed and plotted against the pressure (P) as depicted in Fig. (1) for $CdS_{1-x}Se_x$ for different concentrations. Our calculated lattice constants and phase transition pressure for different concentrations of $CdS_{1-x}Se_x$ alloy. The variation of phase transition pressure and lattice constants with composition(x) is plotted in fig. (2) That shown linear variation between them. The relative volume changes, $\Delta V(P_t)/V(0)$, associated with the above mentioned compression (or phase transition pressure) have also been computed and plotted against pressure to get the phase diagram as shown in fig. (3,4,5,6,7,8 ) for $CdS_{1-x}Se_x$ for different concentration.. The value of these relative volume changes along with other results corresponding to the phase transition pressure ($P_t$) are listed in Table. (B) of $CdS_{1-x}Se_x$ for different concentration and are compared with the available experimental and theoretical data. Predicted phase transitions pressure in fig. (1) has followed a systematic trend approximately similar to those obtained from the experimental observation.

It is thus obvious from the overall achievements that the present three body potential model is adequately suitable for describing the relative stability, prediction of phase transition for $CdS_{1-x}Se_x$ with different concentrations.

**Table (A): Input and Model Parameter for $CdS_{1-x}Se_x$ ($0\leq x\leq 1$)**

| Crystal | Lattice constant a ($A^0$) | $\rho(A^0)$ | b ($10^{-12}$erg) | $f(r_0)$ |
|---|---|---|---|---|
| CdS | 5.82[a] | 0.439 | 2 | -0.011 |
| $CdS_{.8}Se_{.2}$ | 5.866 | 0.4496 | 2.1 | -0.013 |
| $CdS_{.6}Se_{.4}$ | 5.912 | 0.4602 | 2.2 | -0.015 |
| $CdS_{.4}Se_{.6}$ | 5.958 | 0.4708 | 2.3 | -0.017 |
| $CdS_{.2}Se_{.8}$ | 6.04 | 0.4814 | 2.4 | -0.019 |
| CdSe | 6.05[a] | 0.492 | 2.5 | -0.021 |

[a] (O. Madelung et al 1982)

**Table (B): High-pressure behavior of $CdS_{1-x}Se_x$ ($0\leq x\leq 1$)**

| Crystal | Equilibrium Separations ($A^0$) | | Phase transition pressure (GPa) | Relative change in volume (%) |
|---|---|---|---|---|
| | $r_0(B_3)$ | $r'_0(B_1)$ | | |
| CdS Present | 2.81 | 3.03 | 2.99 | 12.33 |
| Exp. | 3.58[b] | 2.72[d] | 2.7[f], 3.1[g] | |
| Other | - | 2.6[c] | 2.57[c] | |
| $CdS_{.8}Se_{.2}$ Present | 2.87 | 3.09 | 2.91 | 12.3 |
| Exp. | 3.62[a] | | | |
| Other | - | | | |

| | | | | | |
|---|---|---|---|---|---|
| $CdS_{.6}Se_{.4}$ | Present | 2.94 | 3.16 | 2.82 | 12.26 |
| | Exp. | 3.65[a] | | | |
| | Other | - | | | |
| $CdS_{.4}Se_{.6}$ | Present | 2.99 | 3.22 | 2.72 | 12.2 |
| | Exp. | 3.67[a] | | | |
| | Other | - | | | |
| $CdS_{.2}Se_{.8}$ | Present | 3.07 | 3.29 | 2.61 | 11.88 |
| | Exp. | 3.7[a] | | | |
| | Other | - | | | |
| CdSe | Present | 3.13 | 3.36 | 2.5 | 11.9 |
| | Exp. | 3.74[b] | | 2.5[h] | |
| | Other | - | | - | |

[a](O. Madelung et al 1982),[b](Urte Hotje et al 2003),[c](J.J. Tan et al 2011),[d](T. Suzuki et al 1983),[f](M. Haase, and A.P. Alivisatos 1992),[g](J.A. Corll 1964),[h](Vladimir V et al 2007)

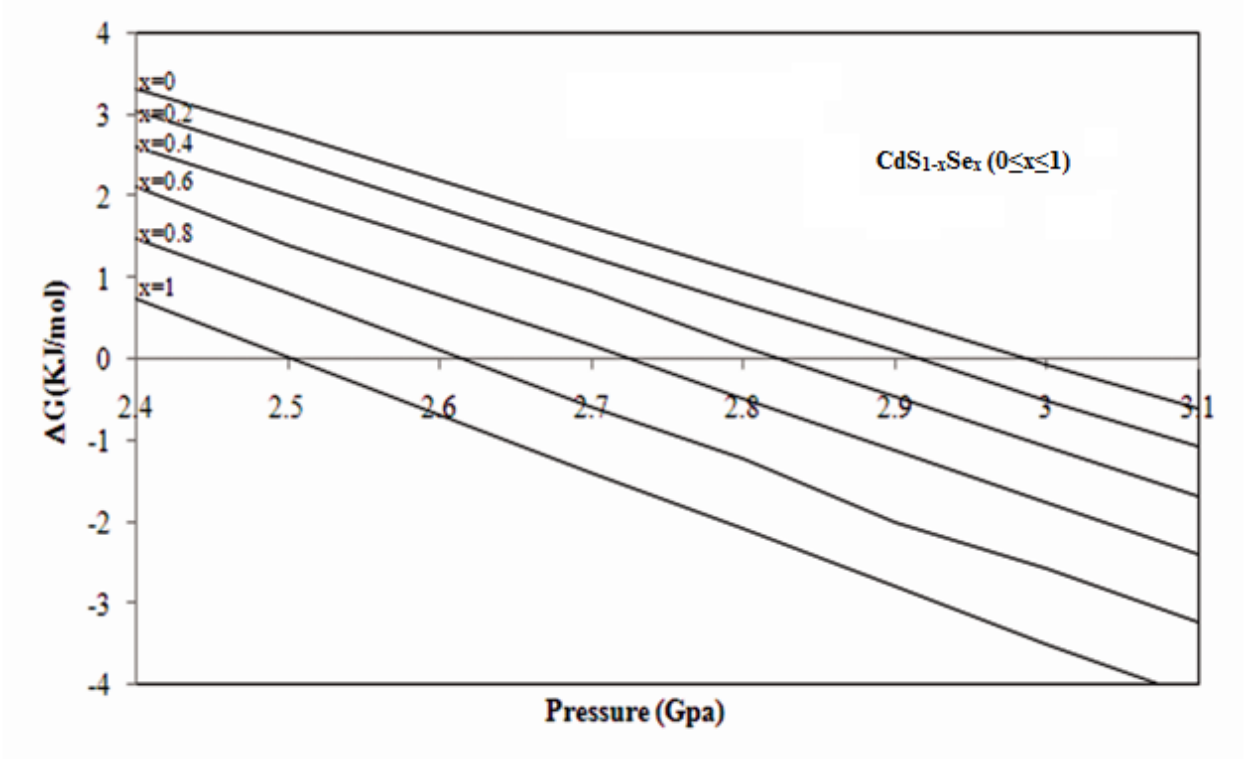


Fig.1 : The Gibbs free energy difference ΔG against Pressure (P) for different concentration x

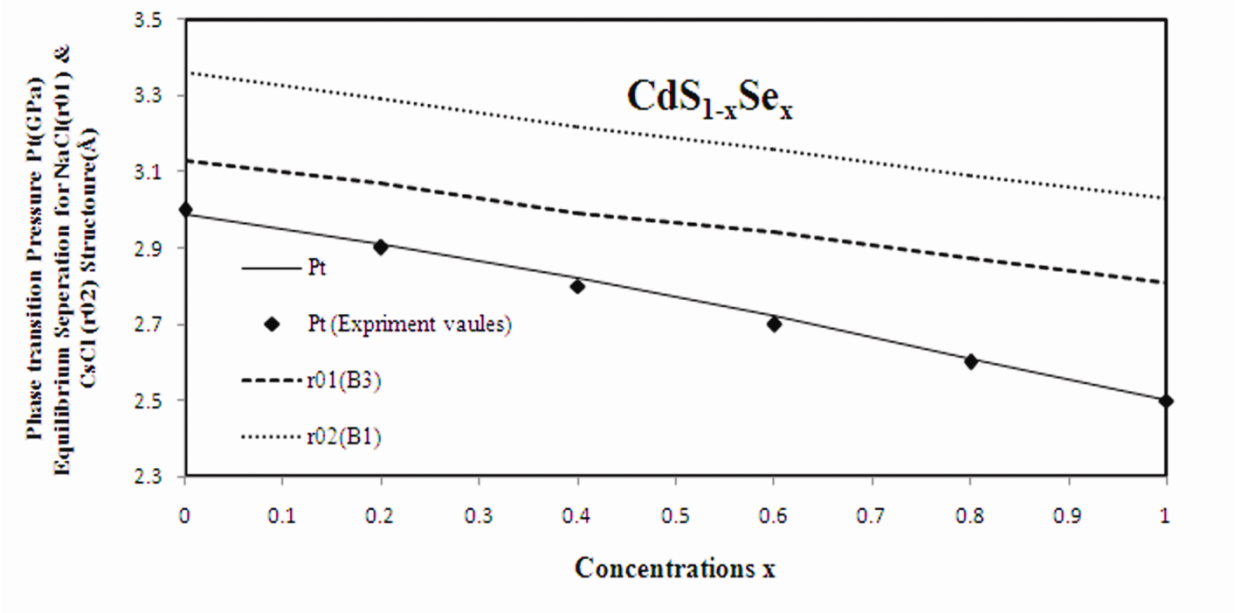


Fig.2 The Variation of Phase transition pressure and equilibrium separation for B3 and B1 Structure with Compositions x

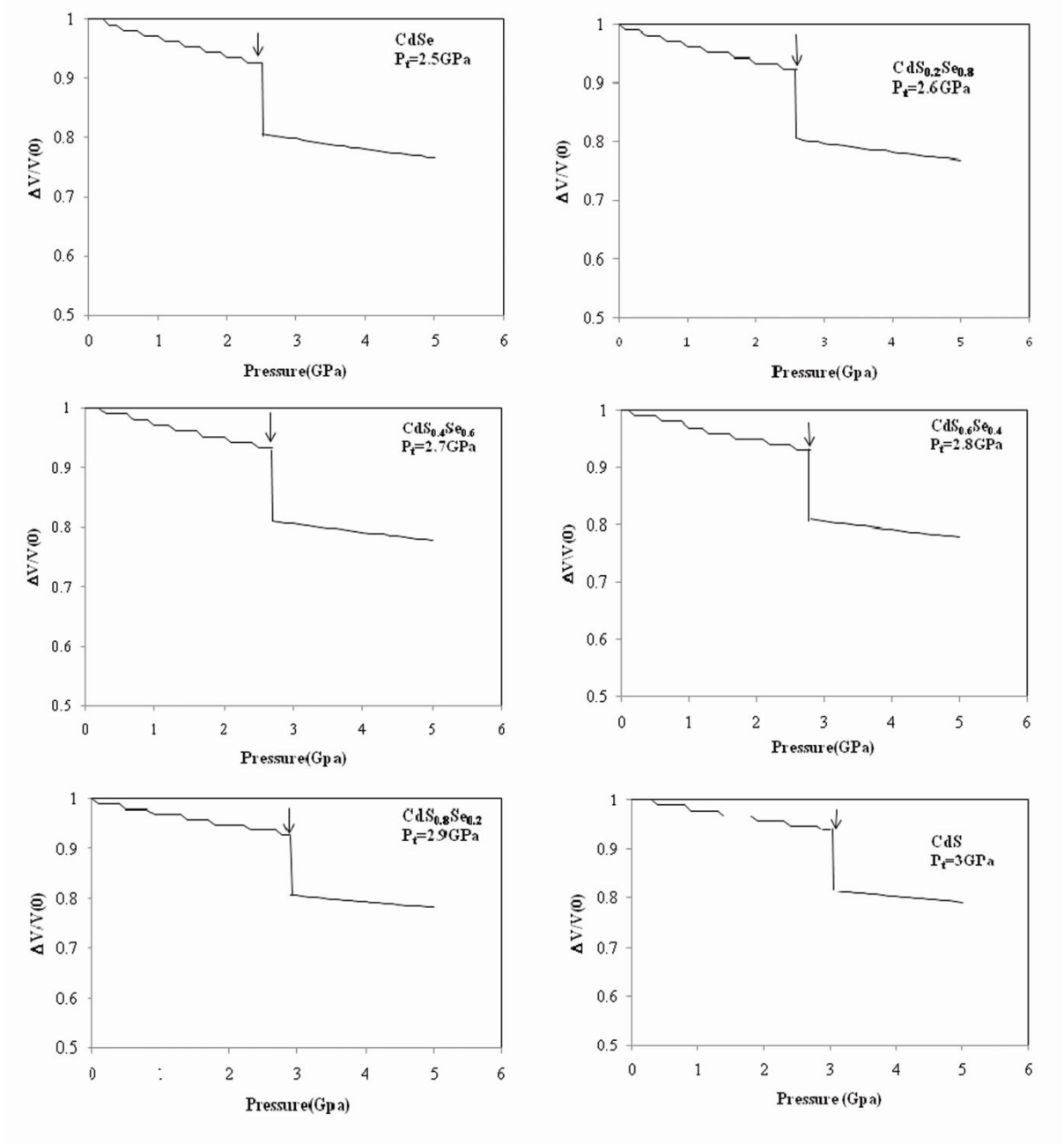


Fig.3 Relative Volume changes Vs Pressure

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