

CHAPTER 6: EFFECT OF DOPING: InP doped with Ga ($\text{In}_x\text{Ga}_{(1-x)}\text{P}$)

The increase in technology has resulted in attempts to uncover credible alternatives for improving the optoelectronic device performances which has led to the study of Group III-V alloys. Also the possibility of controlling the physical properties of these alloys in different composition offers immense scope and advantage resulting in a number of theoretical and experimental studies. Among the III-V semiconductors, InP and GaP have attracted special attention on technological studies. In this chapter, we study the Structural properties, Phase transition and Electronic structure of InP doped with Ga that is $\text{In}_x\text{Ga}_{(1-x)}\text{P}$ alloys for the composition $x = 0, 0.25, 0.5, 0.75, 1$.

6.1. Structural properties and Phase transition

As discussed above in chapter 4, DFT based ab-initio method is used for investigating structural phase transition under induce pressure and electronic structure of InP alloys ($\text{In}_{1-x}\text{Ga}_x\text{P}$: $x = 0, 0.25, 0.5, 0.75, 1$). The alloys are modeled at some selected compositions ($x = 0.0, 0.25, 0.50, 0.75, 1.0$) with structures described in terms of periodically repeated supercells. The minimization of the total energy with respect to the cell parameters give optimized structure, the equilibrium lattice parameter and bulk modulus are obtained fitting to the Birch-Murnaghan equation of states [85]. The energy versus volume curve for both zinc blende (B3) and rock salt (B1) structures at different composition are shown in figure 6.1. The calculated equilibrium parameters are summarized in table 6.1. It is observed that InP for $x=0.0$ and GaP for $x=1.0$ whose comparison data are available and our results are in good agreement.

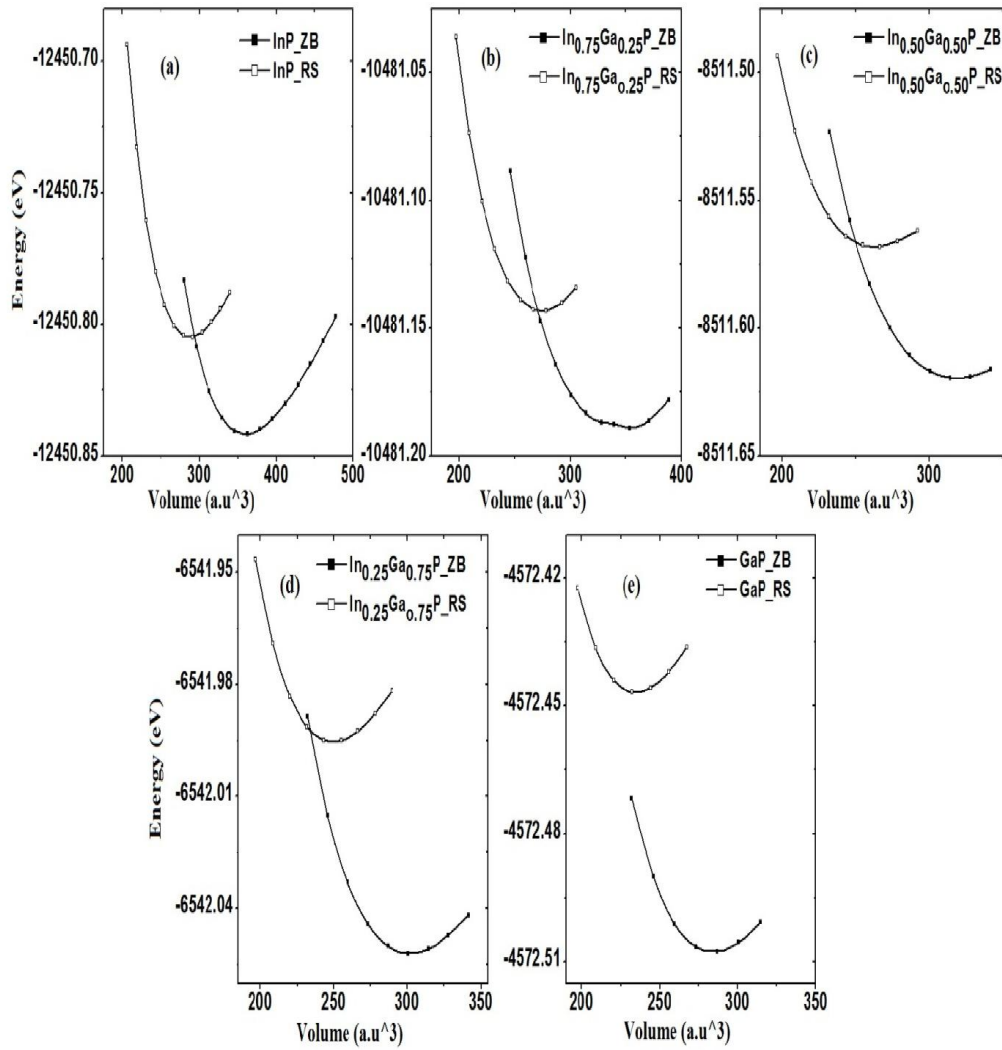


Figure 6.1. Energy versus volume curve of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy within GGA in ZB and RS structure at different concentration of x

Table 6.1. Lattice parameters of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy (in ZB and RS structure) at different concentration of x .

		Zinc Blende			Rock Salt		
		a_0	B_0	B'	a_0	B_0	B'
InP	Present work	5.9	60.5	4.64	5.54	74.78	4.76
	Expt. results	5.90 ^a , 5.87 ^b	65.5 ^d , 72 ^e	4.59 ^c	5.71 ^b , 5.24 ^b	-	-
	Other Theo. results	5.94 ^b , 5.95 ^c	68 ^b , 71 ^f	4.9 ^b , 4.67 ^g	-	-	-
In 0.75Ga 0.25 P	Present work	5.851	65.161	4.424	5.461	76.753	4.600
In 0.5Ga 0.5 P	Present work	5.738	67.722	4.468	5.377	78.496	4.703
In 0.25Ga 0.75 P	Present work	5.633	72.017	4.566	5.288	82.653	4.741
GaP	Present work	5.523	77.70	4.347	5.181	88.303	4.840
	Expt. results	5.47 ^h , 5.50 ⁱ , 5.45 ^j	77.2 ⁱ	4.88 ⁱ	-	-	-
	Other Theo. results	5.41 ^k , 5.54 ^l , 5.51 ^m	90.0 ^k , 76.0 ^m	4.50 ^k , 4.59 ^m	5.165 ⁿ , 5.160 ^o	87.3 ⁿ , 87.59 ^o	3.78 ^o , 4.54 ^o

^aRef[104], ^bRef[105], ^cRef[106], ^dRef[107], ^eRef[108], ^fRef[110], ^gRef[111],
^hRef[82], ⁱRef[84], ^jRef[83], ^kRef 12], ^lRef[85], ^mRef[13], ⁿRef[86], ^oRef[13]

According to Vegard's law [160,161] there is a linear relation between crystal lattice constant of an alloy and composition 'x' at constant temperature.

$$a_{(A_{1-x}B_xC)} = x(a_{AC}) + (1-x)(a_{BC}) \quad (6.1)$$

where a_{AC} and a_{BC} are the equilibrium lattice constants of the binary compounds AC and BC respectively and $a_{(A_{1-x}B_xC)}$ is the lattice constant of the alloy.

For the $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy, we can write

$$a_{(\text{In}_{1-x}\text{Ga}_x\text{P})} = x(a_{\text{InP}}) + (1-x)(a_{\text{GaP}}) \quad (6.2)$$

where a_{InP} and a_{GaP} are the equilibrium lattice constants of the binary compounds AC and BC respectively and $a_{(In_{1-x}Ga_xP)}$ is the lattice constant of the alloy. But deviation in the semiconductor alloys from Vegard's law in experimental [162] and theoretical [163,164,165,166,167] studies resulted in the description of the lattice constant as:

$$a_{(In_{1-x}Ga_xP)} = xa_{InP} + (1-x)a_{GaP} - x(1-x)b \quad (6.3)$$

where the quadratic term 'b' is the bowing parameter.

The Composition dependence of the calculated lattice parameter (A^0) and Bulk modulus (B) within GGA in (a) ZB and (b) RS structure as compared with Vegard's prediction is given in figure 6.2 and figure 6.3 respectively. Our results of the calculated lattice parameter in figure 6.2 shows an almost linear variation with a marginal downward bowing parameter of $0.02823 A^0$ for ZB structure and an upward bowing parameter of $-0.07189A^0$ for the RS structure.

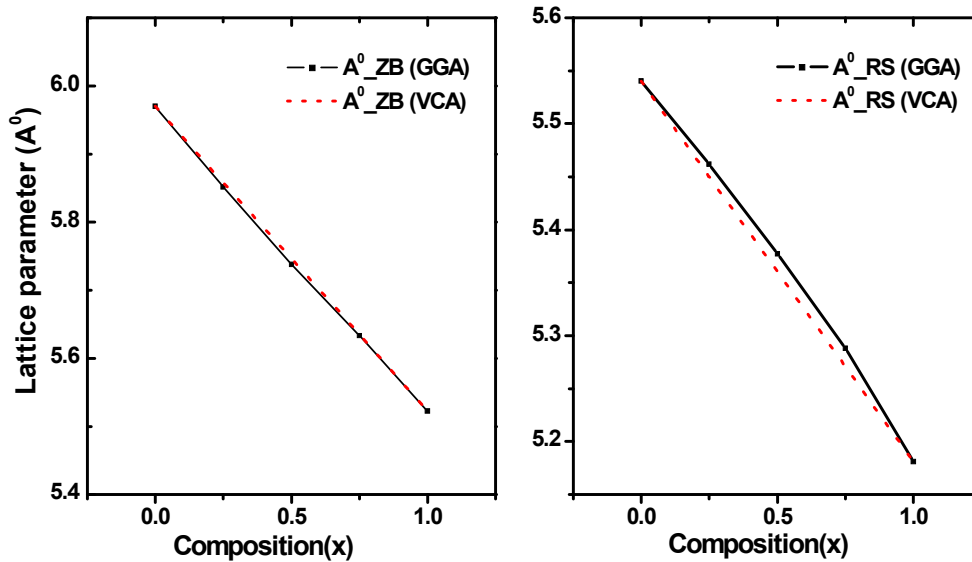


Figure 6.2. Composition dependence of lattice parameter (A^0) within GGA in (a) ZB and (b) RS structure of $In_{1-x}Ga_xP$ alloy as compared with Vegard's prediction.

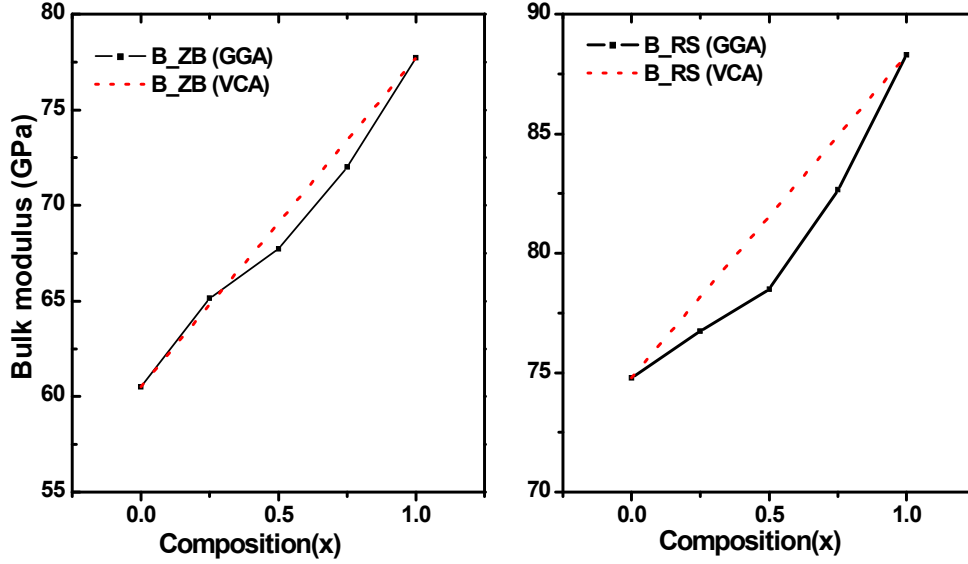


Figure 6.3. Composition dependence of bulk modulus within GGA in (a) ZB and (b) RS structure of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy as compared with Vegard's prediction

For the bulk modulus in figure 6.3 we find that for both ZB and RS structure there is a deviation from the linear concentration dependence with a downward bowing parameter of 4.33704 GPa and 11.1624 GPa respectively. This deviation is mainly due to the bulk modulus mismatch between InP and GaP.

It is clearly seen that the lattice constant of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy linearly decreases while the bulk modulus increases as the concentration of 'x' increases representing the bond weakening or strengthening effects induced by changing the Ga composition in InP. In other sense, the compressibility decreases as the concentration 'x' (of doping Ga atom) increases in InP. Thus it concludes that compressibility from high to low is: $\text{InP} > \text{In}_{0.75}\text{Ga}_{0.25}\text{P} > \text{In}_{0.5}\text{Ga}_{0.5}\text{P} > \text{In}_{0.25}\text{Ga}_{0.75}\text{P} > \text{GaP}$. Thus from InP ($x=0.0$) to GaP ($x=1.0$), it generally becomes less compressible resulting harder InP as compare to GaP. This may be due to lower mass of Ga atom than In atom in the alloy.

The formation energy (E_f) for $\text{In}_{1-x}\text{Ga}_x\text{P}$ has also been calculated by using the following relationship:

$$E_f = E_{\text{In}_{(1-x)}\text{Ga}_x\text{P}} - [(1-x)E_{\text{InP}} + xE_{\text{GaP}}] \quad (6.4)$$

at different concentrations. The calculated formation energies of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy as a function of Ga for zinc blende and rock salt phase are given in table 6.2 suggesting that a phase separation is preferable for this system.

Table 6.2. Formation energies of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (for zinc blende and rock salt phase) alloy at different concentration of x

	Composition	E_f (ZB)	E_f (RS)
In_{0.75} Ga_{0.25} P	0.25	0.070	0.072
In_{0.5} Ga_{0.5} P	0.50	0.055	0.057
In_{0.25} Ga_{0.75} P	0.75	0.039	0.015

The structural phase transition from ZB to RS phase at different composition of x (0.0, 0.25, 0.5, 0.75, 1.0) for $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloys are determined by calculating the Gibbs free energy G. The phase with the lowest Gibbs energy at a given pressure and temperature determines the enthalpy of the phase. As mentioned above (chapter 4 and chapter 5), our calculation is done at zero temperature we e ignored the entropy contribution. Therefore the structural phase transition is calculated from the condition of equal enthalpies i.e. $H = E + PV$. Figure 6.4 shows the variation of Enthalpy with pressure for both the LDA and GGA methods. The enthalpy as a function of pressure at different composition are shown in figure 6.4. The obtained results of transition pressure for different concentration of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy is given in table 6.3.

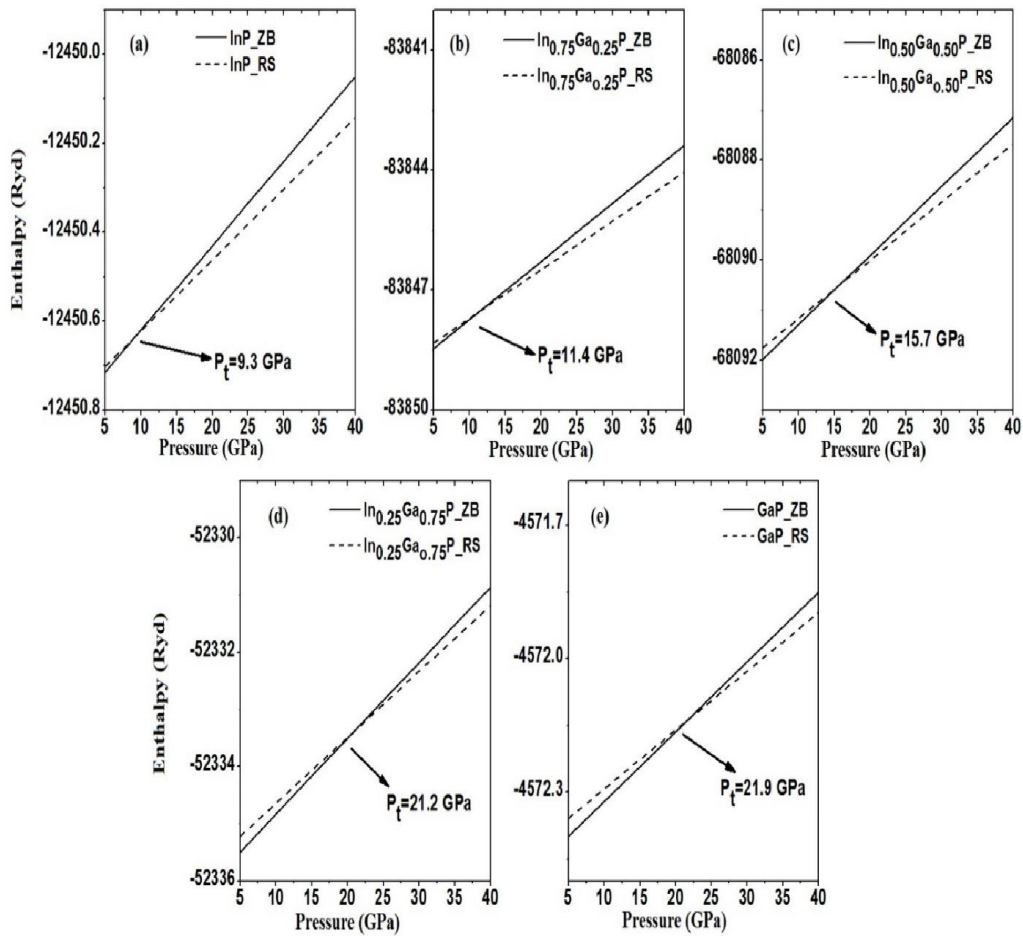


Figure 6.4. Enthalpy versus Pressure of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy at different concentration of x

Table 6.3. Transition pressure of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy at different concentration of x

	Phase transition (P_t) GPa		
	Present work	Expt. Results	Theo. results
InP	9.3	9.5 ^a , 10.3±0.2 ^b , 9.8 ^c	7.3 ^d , 7.5 ^e , 8.5 ^f , 11.0 ^g
In_{0.75}Ga_{0.25}P	11.4	-	-
In_{0.5}Ga_{0.5}P	15.7	-	-
In_{0.25}Ga_{0.75}P	21.2	-	-
GaP	21.9	22 ^h , 24±0.3 ⁱ , 21.5±0.8 ^j	21.7 ^k , 18.8 ^l , 16.8 ^m ,

^aRef[27], ^bRef[28], ^cRef[105], ^dRef[25], ^eRef[112], ^fRef[93], ^gRef[94], ^hRef[87], ⁱRef [88], ^jRef [89], ^kRef [90], ^lRef [91], ^mRef [92]

The present study of transition pressure of InP and GaP are found to be in close agreement with other experimental and theoretical results. In cases where the experimental and theoretical data are not available at concentrations ($x= 0.25, 0.50$ and 0.75), the present result may serve as a reference. In figure 6.4 the phase transition of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloys at different concentration of x ($0.0, 0.25, 0.50, 1.0$) are shown. From the figure, we can clearly see that introduction of Ga at the site of InP increases the transition pressure.

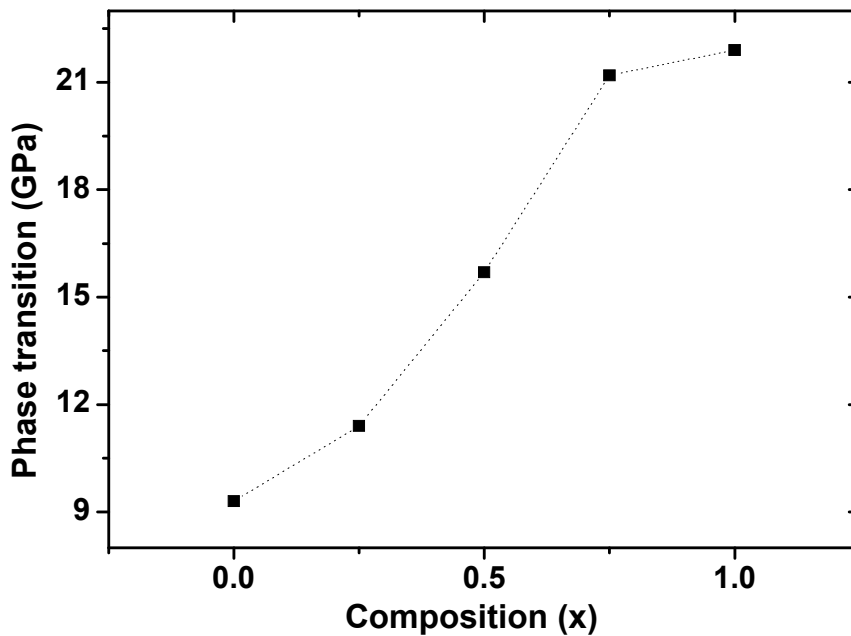


Figure 6.5. Phase transition of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy at different concentration of x

6.2. Electronic Properties

Energy band diagram of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy (in both zinc blende and rock salt structure) are calculated at different concentrations using the obtained equilibrium lattice constant and are shown in figure 6.6 and figure 6.7 respectively.

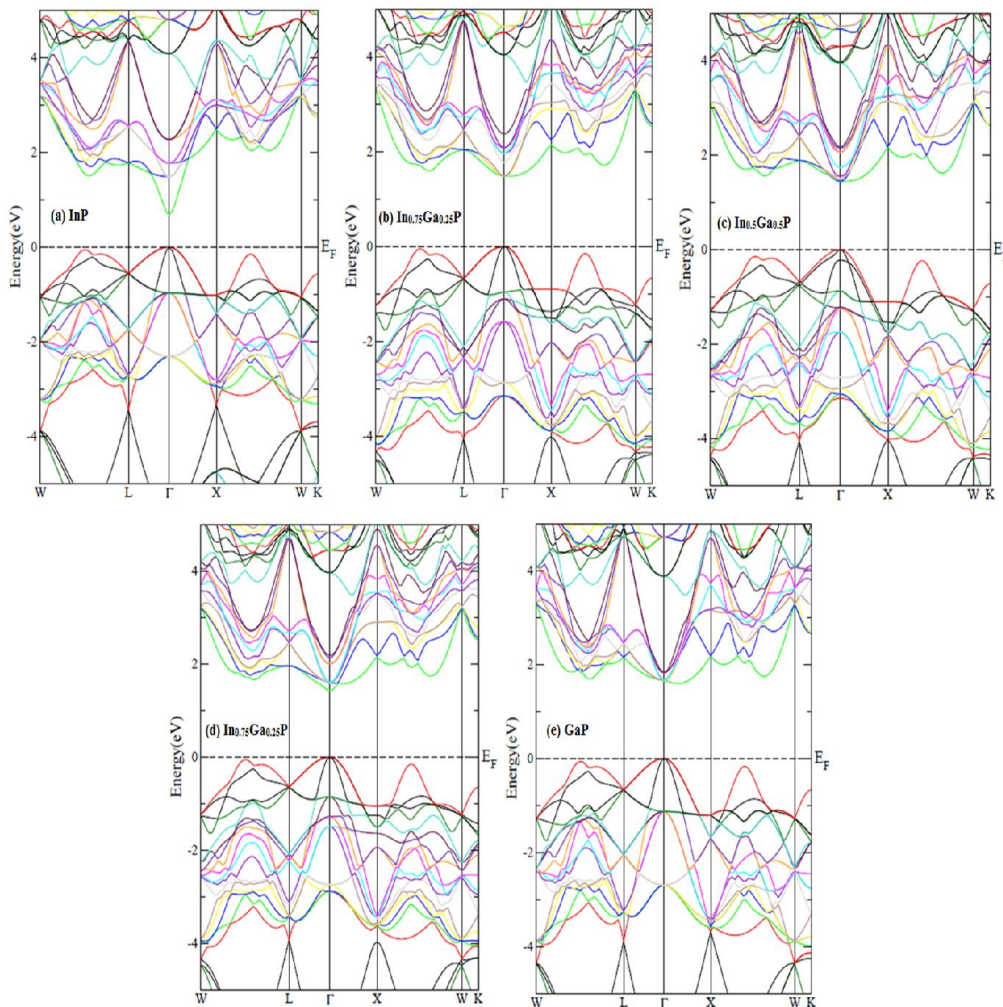


Figure 6.6. Energy band diagram of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (zincblende phase) alloy at different concentration of x

From figure 6.6, we observe that for InP ($x=0.0$) is a direct band gap of 0.58 eV while in case of GaP ($x=1.0$), is an indirect band gap of 1.56 eV. This has also been discussed earlier in chapter 4 [25,88,107,116]. It is noted that with increase

in concentration of x (0.25, 0.5, 0.75) in $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy, the direct band gap is found to increase upto a concentration of 0.25 but as the composition of ' x ' increases it starts decreasing. The band gap of present study of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (zinc blende phase) alloy at different concentration of ' x ' are compared with other available experimental, theoretical data and are shown in table 6.4. Our results are found to be smaller than the experimental results which are expected as GGA calculation within DFT generally underestimates the energy band gaps. This decrease in the band gap may be due to structural relaxation of the alloy and charge exchange that are respectively proportional to the difference in the atomic orbital sizes. Finally at a concentration of $x=1.0$, $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy becomes in its pure form of GaP that becomes indirect as discussed above. This transition from the direct to indirect band gap is due to strong hybridization of the Ga and In with P which results in the splitting off of the conduction band at the Γ point producing another conduction band minimum between the Γ -X points resulting in an indirect band gap. The transition from the direct to indirect energy band gap may also be explained in terms of the ordering induced evolution of band states at high symmetry points and their consequent folding into the same symmetry states in the ordered ternary alloys [168]. In Figure 6.7, the energy band diagrams of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (rock salt phase) alloy at different concentration of ' x ' show crossing over of the conduction band and the valance band at the Fermi energy thus indicating metallic character of the $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy (in rock salt structure) at all concentrations of x .

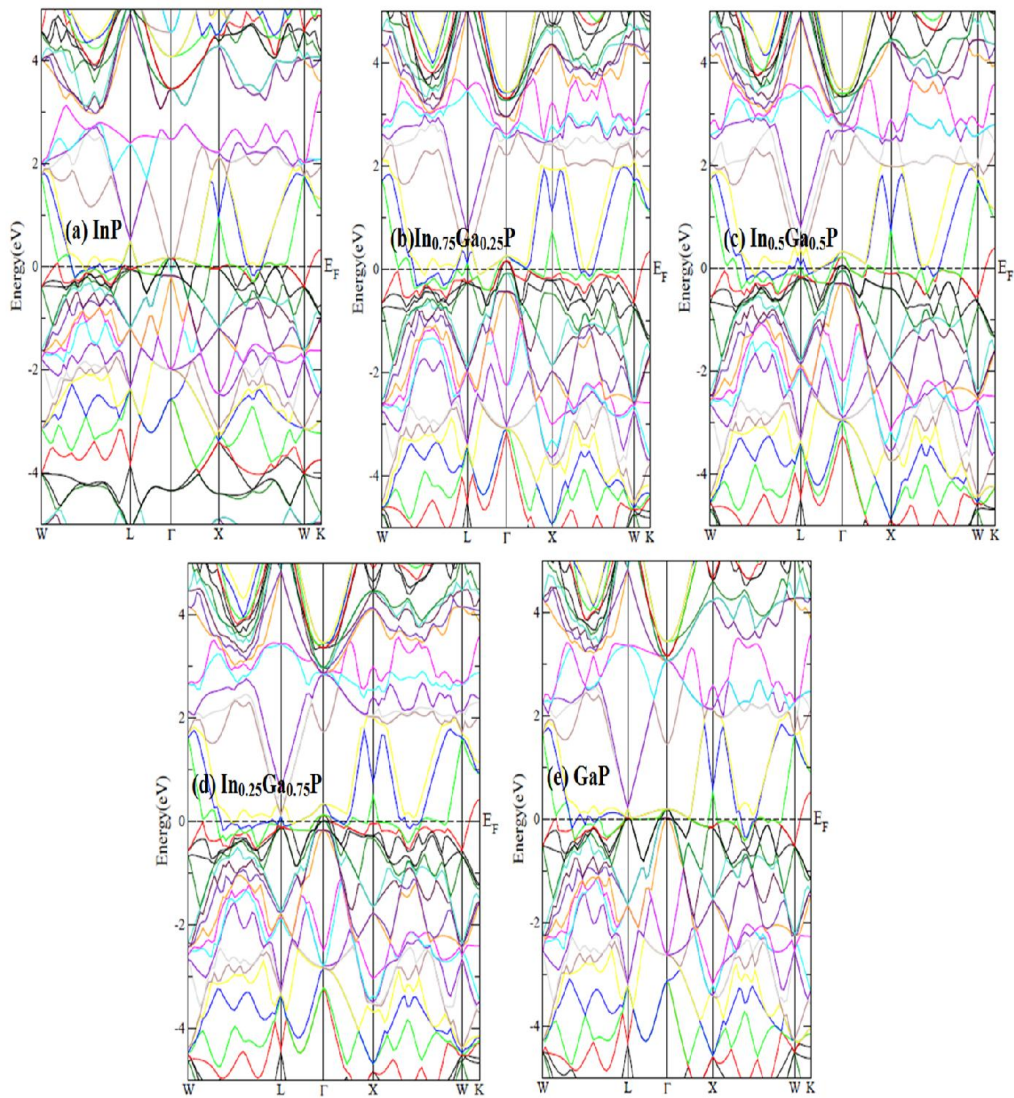


Figure 6.7. Energy band diagram of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (rocksalt phase) alloy at different concentration of x .

Table 6.4. Calculated energy band gap of $\text{In}_{(1-x)}\text{Ga}_x\text{P}$:

	Concentration (x)		Energy Band Gap
InP	0.0	Γ - Γ	0.58 (direct)
In_{0.75}Ga_{0.25}P	0.25	Γ - Γ	1.46 (direct)
In_{0.5}Ga_{0.5}P	0.50	Γ - Γ	1.44 (direct)
In_{0.25}Ga_{0.75}P	0.75	Γ - Γ	1.37 (direct)
GaP	1.0	between Γ -X	1.56 (Indirect)

To further understand the effects of atomic relaxation on the electronic band structure of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (zinc blende phase) alloy, the total density of states (TDOS) and partial density of states (PDOS) are calculated and shown in figure 6.8(a, b, d, e). For the compound InP ($x=0.0$) we see that p state (of P atom) is concentrated at the valance band minimum (VBM) while the conduction band minimum (CBM) is mainly formed by the s state (of In atom) and p state (of P atom). When the concentration $x=0.25$ of Ga atom is doped in InP, we find a presence of p state (of Ga atom) along with the p state (of P atom) in the VBM, while in the CBM there is an equal contribution of the s state (of Ga atom) and s state (of In atom) but replacement of the Ga atom in the In atom causes shifting of the states towards higher energy resulting an increase in the energy band gap. As the concentration of Ga ($x=0.5$) increases there is a push in the s orbital (of Ga atom) in the CBM towards the Fermi energy causing reduction in the energy band gap with the VBM fixed. More increase in the concentration of Ga ($x=0.75$) causes all s state (of Ga atom) and s state (of In atom) to push towards the Fermi energy further reducing the energy band gap to 1.37 eV. We also see that as the concentration of 'x' increases, the contribution of the s state (of Ga atom) in the CBM increases while the p state (of P atom), p state (of Ga atom) and p state (of In atom) becomes more concentrated towards the VBM. Finally when all the In atoms are replaced by the Ga atom, we find that in the CBM the s state (of Ga atom) and p state (of P atom) increases along with the p state (of Ga atom).

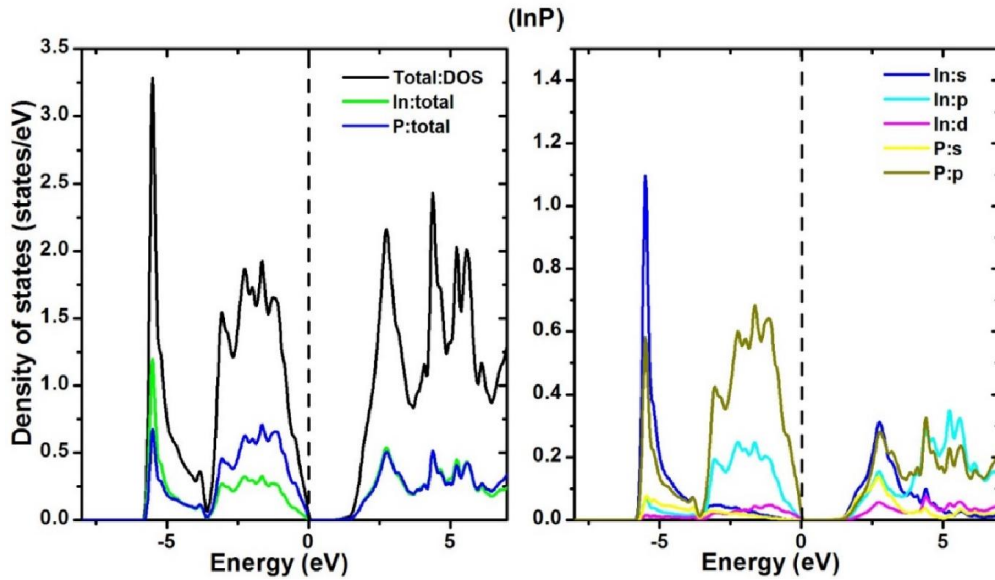


Figure 6.8(a). Total and partial DOS of InP-zinc blende phase

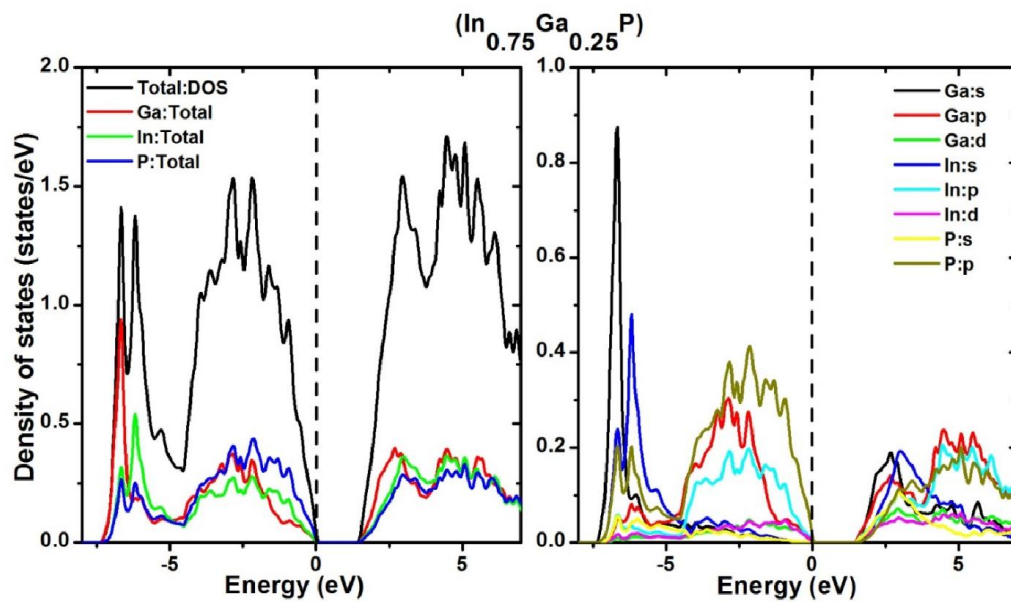


Figure 6.8(b). Total and partial DOS of In_{0.75}Ga_{0.25}P-zinc blende phase

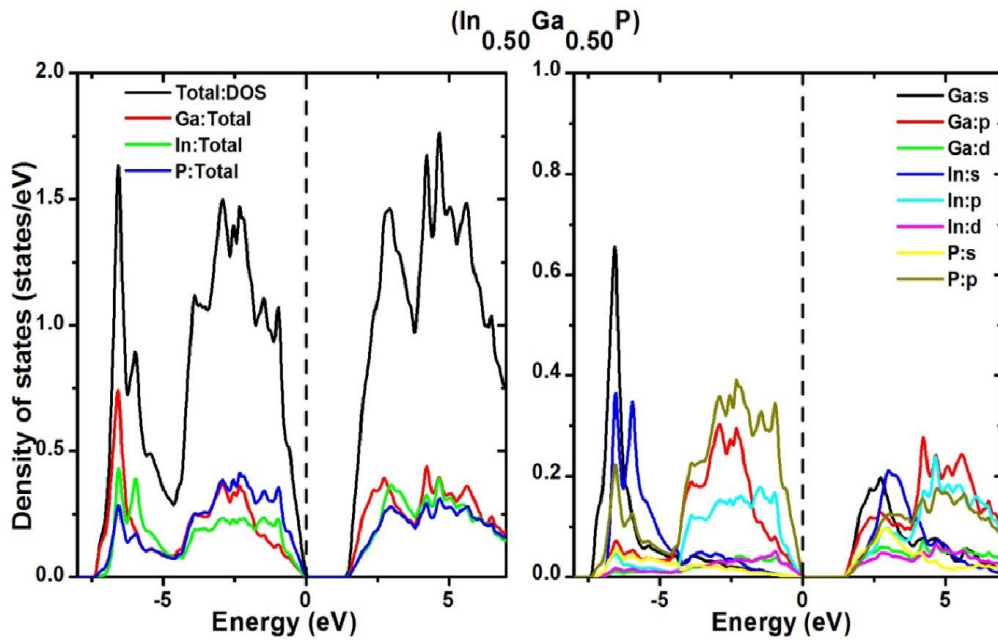


Figure 6.8(c). Total and partial DOS of $\text{In}_{0.50}\text{Ga}_{0.50}\text{P}$ -zincblende phase

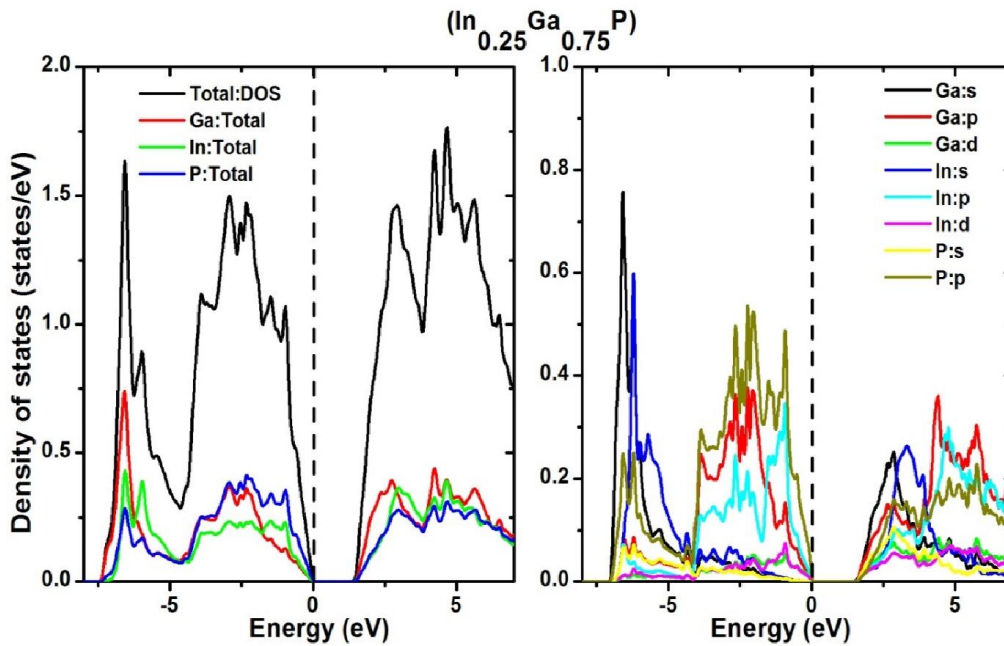


Figure 6.8(d). Total and partial DOS of $\text{In}_{0.25}\text{Ga}_{0.75}\text{P}$ -zinc blende phase

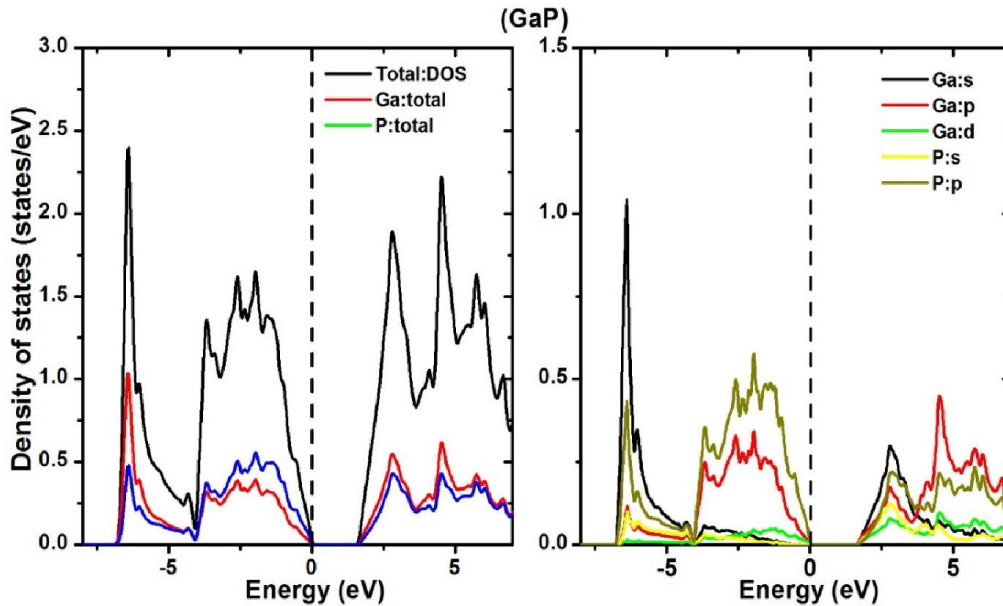


Figure 6.8(e). Total and partial DOS of GaP-zinc blende phase

6.3. Conclusion

The structural and electronic properties of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy (in both zincblende and rocksalt structures) are studied at different concentration of Ga atom ($x = 0.0, 0.25, 0.50, 1.0$).

- i. The composition dependence of the lattice constant and bulk modulus in both the phases are calculated and found to have a linear dependence obeying Vegard's law.
- ii. The bulk modulus of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy increases with increasing concentration of Ga atom which indicates larger in the strength of the alloy and thus makes it less compressible.
- iii. The formation energy at different concentrations of 'x' for both the phases are also calculated. The phase transition from zincblende to rocksalt phase for the alloy with different doping concentrations of Ga are also studied and transition pressure is found to increase with increasing concentration.

- iv. The study on the energy band gap of $\text{In}_{1-x}\text{Ga}_x\text{P}$ (zincblende phase) alloy shows a non linear behavior with concentration. We find that the direct energy band gap of InP increases as the concentration of Ga atom increases upto 0.25. After that it starts decreasing with concentration ($x=0.5, 0.75$) and finally it becomes indirect band gap of GaP at $x=1.0$.
- v. The DOS study confirms that doping of Ga atom increases the energy band gap with respect to InP compound as predicted in energy band diagrams.
- vi. For $\text{In}_{1-x}\text{Ga}_x\text{P}$ (rocksalt phase) alloy at different concentration of 'x' shows crossing over of conduction band and valance band at Fermi level thus showing metallic character of the $\text{In}_{1-x}\text{Ga}_x\text{P}$ (rocksalt phase) alloy at all the concentrations of 'x'.