Chapter 5
Summary and Conclusion

5.1 Summary

Nanomaterials exhibit many promising characteristic properties in terms of their mechanical, thermal, transitional and electronic behaviors as compared to the respective bulk materials. In recent years considerable attention has been paid to the study of nanomaterials. Since the two thermodynamic parameters (i) pressure and (ii) temperature are very sensitive to nanomaterials, the high pressure study of nanomaterials provides a possible path for making availability of solid state materials. The phase transformation and instability properties of such materials constitute a straight path for the discovery of new nanomaterials. It is observed that under high pressure, the nanomaterials show very interesting properties because of the facts that: (i) the atomic interactions between nano-object and pressure transmitting medium are modified, (ii) phase transition from one phase to another phase occurs, and (iii) transformation of the interactions between nano-object due to drastic change in surface-volume ratio of atoms. The pressure is attractive thermodynamical variable to explain several mechanical properties of most of the nanomaterials and their composites. This is why the pressure induced studies on nanomaterials have been a subject of research interest.

In chapter 1, the review of literature with a brief description of nanomaterials is discussed. The critical survey of available literature on nanomaterials shows that the experimental studies on high pressure compression in nanomaterials are available adequately. However, the theoretical studies have been quite scarce. Though, the several experimental investigations have been performed on the nanostructured materials, yet very less effort are made to verify the experimental investigations on the basis of theoretical models. So, there is a need of a simple theoretical model which could provide a comparative and complementary method to analyze the compression and stability
behavior of nanomaterials under high pressure. In the present research work the theoretical study of nanomaterials for which the experimental data available is carried out using the equations of state based on the thermodynamic variables. The main objective of the present research work is to provide a simple, comparative and complementary method to analyze the compressional behavior and stability of nanocrystals under high pressure.

In chapter 2 of the present thesis, the author has described the theoretical approach based on the potential independent model (Usual Tait’s equation of state) to explain the pressure dependent properties of fullerites and carbon nanotubes. The Usual Tait equation of state is used for the study of mechanical properties of fullerites and carbon nanotubes. It is found that the percentage deviations obtained in volume compression at highest pressure are less using Usual Tait eq. (2.67) for C_{60}, C_{70}, C_{84} solids, carbon nanotubes individual, carbon nanotubes bundles, Ni-filled multiwalled carbon nanotubes (MWCNT), Fe-filled MWCNT, and α-Fe filled nanotube which justifies the suitability of eq. (2.67) as compared to other equations of state. The variation in bulk modulus as the function of pressure is also evaluated using Tait’s equation (2.68) for Carbon nanotube individual and Carbon nanotube bundles. The results obtained from equation (2.68) are shown in figures 2.4(b), 2.5(b). It is found that the bulk modulus increases on applying pressure on carbon nanotubes which verifies that the Tait equation of state successfully explains the elastic properties of fullerites and carbon nanotubes under high pressure.

In chapter 3, the analysis of the first order structural phase transition pressure in ZnO, AlN, CeO₂, ZnS and ZnSe nanostructures is performed using the Tait equation of state. In the present work, the pressure dependent second order elastic constants (SOEC) are also calculated for ZnS and ZnSe nanostructures using a potential independent model and mechanical instability of these nanostructures is verified using the mechanical stability criteria for a cubic crystal. The pressure dependent second order elastic constants (SOEC) for γ-Si₃N₄ nanocrystal are calculated and mechanical stability of the nanocrystal is judged. The phase transition pressure obtained using the Tait's equation (2.67) for ZnO nanowire, ZnO nanorod, ZnO nanocrystal are 22.4 GPa, 17.2 GPa and 10.5 GPa respectively. The results are reported in figures (3.1-3.3) along with the experimental data which show that the transition pressure decreases as the volume compression increases.
during the transformation of material from hexagonal wurtzite (B4) phase to the cubic rock salt (B1) phase. The phase transition pressure values predicted from the Tait's equation (2.67) are 14.6 GPa and 22.5 GPa respectively for AlN and CeO$_2$ nanostructures. The phase transformation from B3 phase to B1 phase occurs at 19.67 GPa pressure in ZnS and 13.6 GPa in ZnSe nanostructures. The results achieved here in these nanostructures are reported in Table 3.2. The results achieved here in these nanostructures are found very close to the experimental values which demonstrate the validity of the present approach. Further, the pressure dependent second order elastic constants (SOEC) are calculated for ZnS and ZnSe nanostructures using a simple approach using equation (3.4). The variations of elastic constants C$_{11}$, C$_{12}$ and C$_{44}$ with pressure P are shown in figure 3.6(c) and figure 3.7(b) for ZnS and ZnSe nanostructures. Using the mechanical stability criteria for a cubic crystal as deduced by Sinko and Smirnov [118]; the mechanical instability of ZnS and ZnSe nanostructures has also been verified and the results obtained are shown in figures 3.6 and 3.7. Also, the compressional behavior and elastic constants for $\gamma$-Si$_3$N$_4$ nanocrystal has been analyzed under pressure in terms of the calculated values of elastic moduli, $\delta_{011}$, $\delta_{012}$, and $\delta_{044}$ using equation (3.4). The results are reported in figures 3.8 (b), 3.8 (c) and 3.8 (d) and are compared with those determined by previous investigators using the different theoretical approaches [65]. The trend of variation of elastic constants C$_{11}$, C$_{12}$ and C$_{44}$ vs. pressure is found same as the previous results obtained by using the LDA and GGA theoretical approaches [65] and the mechanical stability of $\gamma$- Si$_3$N$_4$ nanocrystal has been verified up to 68 GPa pressure. A single equation of state can thus explain the mechanical properties of bulk materials and nanomaterials with the same potential.

Though the usual Tait’s equation of state explains the results of volume compression for most of the nanomaterials successfully, however, in some of the nanomaterials, like 3C- SiC (30 nm), Rb$_3$C$_{60}$, Zr Ti$_{17}$O$_{16}$ (40 nm), Zr$_{0.1}$Ti$_{0.9}$O$_2$ (40 nm), TiO$_2$ (rutile phase), TiO$_2$ (anatase phase), SnO$_2$ (14 nm), SnO$_2$ (3 nm), $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, $\gamma$-Al$_2$O$_3$ (37 nm), $\gamma$-Al$_2$O$_3$ (67 nm), MgO (100nm), Ni (12.4 nm), Ni (29 nm), Fe-Cu (14 nm), Ag (10nm), CdSe (rocksalt phase), CuO (24 nm), $\varepsilon$- Fe Hexagonal Iron, Ge (13 nm), Ge (49 nm), Mo, Au (30nm) etc, the Tait’s equation predicts the results accurately only when its modified and extended form is used. Therefore, we have expanded and extended
the equation further and then applied it to determine the volume compression in many other nanomaterials. In chapter 4, we have used both the usual and extended forms of Tait equation of state for the study of volume compression in nanomaterials. The input data required are listed in Table 4.1. The calculated values of pressure $P$ corresponding to different values of compressions $V/V_0$ at $T = T_o$ from usual Tait eq. (2.67) and its extended forms eq. (4.4) and eq. (4.5) are reported in figures 4.1 - 4.25 along with the experimental data for the purpose of comparison. We have considered only those nanomaterials for which the experimental data of $V/V_0$ versus pressure are available so that comparison could be made easily. There is a good agreement between theoretical work and experimental data for the materials considered in the present work. It is important to mention here that the results obtained from extended forms of Tait equation of state, i.e., equation (4.4) and equation (4.5) are close to experimental data in comparison to the results obtained from Tait eq. (2.67). Also, the percentage deviations calculated at highest pressure in volume compression are less using modified formulations. The percentage deviation calculated in volume compression at highest pressure using eq. (2.67) and its modified forms eq. (4.4) and eq. (4.5) are reported in Table 4.5, which clearly indicates that the modified equations of state yield the results more close to the experimental values and is better than the Tait equation of state for the study of compressional behavior of nanomaterials.

5.2 Conclusions and Future scope

The study of nanomaterials under high pressure is found to be an attractive and wide area of research having lot of applications in both applied sciences and nanotechnology. In the present research work, the Usual Tait’s EOS (eq. 2.67) is found to be the best equation for the study of mechanical properties of fullerites and carbon nanotubes. The Tait’s equation of state successfully explains the phase transition and elastic properties of nanomaterials. However, the modified forms of this equation of state are useful for studying the high-pressure compression behavior of nanomaterials. To demonstrate the validity of the formulated equation of state, we have employed the modified Tait’s equation to compute the pressure dependence of volume compression in twenty-five nanomaterials. A good agreement between calculated and experimental data
is reported in the present work. The major advantage of the equation of state is that it follows the basic laws of thermodynamics with regard to relations at high pressure and also permits extrapolation to regions for which experimental data are not available. We have thus reported a simple and straight forward potential independent approach to study the elastic behavior and mechanical stability of nanomaterials under high pressure.

On the basis of overall descriptions, it is stated that the high pressure study may be helpful for planning high pressure experiments on the compression behavior of nanomaterials. The elastic properties like the shear modulus and bulk modulus which show the behavioral change of nanomaterials as compared to their counterpart bulk materials can also be calculated and compared with the available experimental data. It may thus be emphasized that the high pressure study of nanomaterials is an appealing, young and higher expanding area for both applied and fundamental investigations.