Chapter 1
Introduction

1.1 Overview

During 21st century the nanotechnology has been the turning point for the revolutionary development in the fields of science and technology. The study of nanomaterials under high temperature has the potential to explore the path to fabricate the materials by assembling the atomic structure in controlled way. Nanotechnology established by National Nanotechnology Initiative (NNI) is defined as the manipulation of matter with restricting the size of the matter between 1nm to 100 nm and referred to nanoscale technology. It is also defined as a branch of engineering that deals with manufacturing and exploring the electronic circuits and mechanical devices at molecular level. The concept of nanoscience and technology was first discussed in 1959 by physicist Rechard Feynman in his talk ‘there is plenty of room at the bottom’ in which he described the direct manipulation of atoms which are possible to be synthesized. The term nanotechnology was used by Noria Taniguchi in 1974 for the first time in history and claimed that scientist has acquired the ability to see or to manipulate matter at nanometer scale.

The invention of Tunneling Electron Microscope (TEM) and Scanning Electron Microscope (SEM) during 1980-81 opened up the new way of nanotechnology. The discovery of these two optical electron microscopes has provided unpredictable or unexpected visualization about the individual atoms or molecule and motivated the inventors to develop the bottom-up technique to synthesize the nanomaterials. In 1985, H.W. Kroto et al. [1] discovered the structure of bucky ball known as fullerene. The fullerene consists of 60 carbon atoms linked together to form a cage like structure [2] which has 20 hexagons bonded with 12 pentagons through Vander Waals forces. The molecular structure of fullerene has the symmetry like a soccer ball and consists of $sp^2$ like bonding structure. The fullerene further lead to the discovery of carbon nanotubes which have great technological importance in the fields of engineering and medical science.

The nanominerals play the important role in understanding the dynamics and evolution of lower mantle of earth under high temperature and pressure. The study
of minerals at high temperature and high pressure are, therefore, important to know about the science of earth interior. The physical properties like thermal conductivity, electrical conductivity, thermal expansion, specific heat, bulk modulus properties etc. show the interesting behavior of nanomaterials and nanominerals under high temperature. It is, therefore, important and necessary to analyze the thermal properties of nanomaterials in order to make their uses in nanodevices to measure the various physical properties under high temperature without damaging the shape and size of the materials.

Foresterite (Mg$_2$SiO$_4$) and Faylite (Fe$_2$SiO$_4$) are two minerals simply known as olivine. Faylite is rich in iron whereas Foresterite is magnesium rich mineral. Foresterite is found in ultra igneous rocks or in marbles and in iron-nickel meteorites. The study of these minerals under high temperature is essential because their temperature and pressure dependent data are very important and significant for investigating the deep study in the field of earth science. Rheological properties of minerals are strongly depending on grain size [3]. Though the physical properties of earth minerals (bulk) having size structure between micro and millimeter range are studied extensively, yet the theoretical study of nanominerals is still needed for further exploration.

Nanocrystalline Zirconia powder is grown with fairly narrow particle size using amorphous citrate route by Bhagwat and Ramaswamy[4]. The crystalline size is determined from XRD and a close agreement of particle size is also determined by TEM. It is noted that the inter-atomic separation increases with increasing temperature which indicates that the zirconia is not as rigid as other nanocrystals. However, the rigidity of zirconia nanoparticle is larger than that of its bulk crystal.

Zinc oxide(ZnO) is the semiconducting ionic crystal and shows the rapid change in thermal expansion with temperature at high rate[5]. At extreme conditions ZnO has wurtzite structure that transforms into rocksalt at high pressure, however, on decreasing the pressure it reverts back into wurtzite structure. Petre et al. [5] and Seelaaboniya et al.[6] have studied the thermal expansion and elastic behavior of ZnO-rocksalt under high temperature. They found that the elastic constants and the thermal expansion coefficient increases with increasing the temperature in ZnO-rocksalt phase whereas in wurtzite phase this increment is very slow. There are
tremendous applications of zinc oxide like in UV laser, transparent conducting films and sunblock coatings etc.

TiO₂ being a semiconductor and having wide energy band gap of 3.2 eV is an optical material due to its large refractive index. It exists under earth mantle in polymorphs form and most common natural polymorphs are rutile, anatase, and brookite anatase are in metastable while rutile is in stable phase. It has potential applications in electronics and mostly in nitrogen fixation to produce hydrogen gas.

The study of thermal properties of n-nickel oxide has also attracted the attention of investigators because it has many applications in microelectronic packaging. It has useful magnetic and optical properties like the optical fibers which help in exploring the different types of nanocomposites like aluminium composite and nanopolymers used in electronic communication. Aluminium composites are used in field emission devices due to its high rigidity and high thermal conductivity. The nanometals like Silver(Ag) and Gold(Au) have unique optical, electrical and thermal properties under high temperature and high pressure. The electrical and thermal conductivities of these metals increase with temperature unlike in bulk silver and gold metals though their thermal expansion coefficients do not change significantly as compare to bulk metals. The most common use of silver and gold nanoparticles is made for antimicrobial coatings, wound dressing, drug delivery system and biomedical devices.

Graphene has a negative thermal expansion coefficient as a function of temperature ranging from 0-900K (13nm). Mounet et al.,[7] determined the thermal expansion coefficient to graphene by using the first principles calculation and predicted that graphene has a negative TEC at least up to 2500K[7]. Bao et al.,[8] experimentally obtained the TEC in temperature range of 300-400K by monitoring the small change in the sagging of a graphene piece suspended over a trench and estimated that it is negative only up to 350K. However, it is not clear that the discrepancy between theory and experimental data arises due to the uncertainties in the experimental measurements or limitations in the theoretical calculations. In the present work we have used a simple theoretical model based on temperature dependent equation of state (EOS) to estimate the volume expansion and thermal expansion coefficient(TEC) of graphene over the temperature range 300K-1000K.
The results achieved in the present study are found very close to the experimental data which justifies the applicability of our model theory to explain the negative thermal expansion behavior of graphene under high temperature.

1.2 Effect of Temperature & pressure on nanomaterials

The physical and chemical properties of nanomaterials depend upon mainly on the surface area of grain boundaries where the large number of atoms about 80% of total number lying on the surface unlike in bulk materials where only 15% to 20% atoms remains at the surface. Due to the grain boundaries and large surface-volume ratio in nanomaterials they show very different and anomalous behavior under high temperature and high pressure as compared to their counterpart bulk materials. The strength and elastic properties of such materials also depend upon the inter-atomic bonding between the atoms. Under high pressure and high temperature the nanomaterial structure is generally changed and transform to different phase structure because of the change in inter-atomic separation between the grains remain at the boundary of the material. This is why the nanomaterials show the anomalous behavior under high pressure and high temperature.

The temperature and pressure dependent properties of nickel (n-Ni) metal have been the subject of considerable interest during past years [9-11]. Nickel is a transition ferromagnetic 3d metal that is widely used as catalyst at extreme conditions. To understand the properties of nickel, the grain boundaries structure has been widely studied by using the transmission electron microscope (TEM), X-ray diffraction (XRD) and inelastic neutron scattering techniques.

The study of thermo-mechanical properties of graphene has also been of great interest due to potential applications in electronic materials[12-14] as well as its exceptional properties[15-17]. Its high thermal conductivity and extremely high mechanical strength make it an important candidate material for heat control in electronic devices. The experimental studies show that the strain of a graphene sheet placed on a substrate is found much larger than for graphene suspended in air. The two main theoretical models based on thermo-elastic theory and the empirical inter-atomic potentials have predicted the thermo-physical properties measured in compressing and stretching experiments[18-20]. It is noted that the elastic theory does not give the atomic features of graphene while the empirical
potentials such as the Brenner potential [21,22] valence force and the LCBOPPII potential [23] can properly account for the thermo-elastic properties of graphene.

1.3 Issues and Challenges

During last decade, many theoretical and experimental studies have been performed to analyze the various thermo-physical properties of nanostructured crystals and minerals under high temperature. The theoretical models described earlier are, generally, based on the uncertainty of the potential parameters and therefore, yield not only the computational complexity in calculations but also sometimes inaccuracy in the results. In the present investigation we have employed the potential independent equation of state (EOS) which consists of only two input thermodynamic variables and provides a simple method to predict the thermo-elastic properties of nanomaterials under the effect of high temperature and high pressure.

The equation of state (EOS) provides the pressure-volume-temperature relationship to analyze the thermal &elastic properties of solids with different crystal structure. The importance of EOS can be ascribed to the fact that the equation of state can predict extrapolation and interpolation values especially where the experimental data are not readily available. The equation of state also helps in future planning for the fabrication of high temperature scientific and engineering devices. Most of the equations of state used earlier for bulk materials such as Vinet et al.[24], Shanker et al.[25], Suzuki et al. [26], Poirier and Tarantola et al. [27] and Hama and Suito et al. [28] are not found fit to produce the satisfactory results of thermo-elastic properties over the different ranges of temperature. The experimental and theoretical studies have been highly valuable and beneficial for determining the structural and other related physical properties of nanocrystalline materials under high temperature and high pressure. The nanocrystalline materials having size from 1nm to 100nm show the anomalous behavior of thermal expansion properties because of the fact that the nanomaterials have large surface–volume ratio and grain boundary effects.

Murnaghan [29] had derived the basic equation of state (EOS) assuming that the bulk modulus is a linear function of temperature at constant pressure. The
Murnaghan’s EOS has been very successful to explain the thermo-physical properties of bulk materials and the results are reported close to the experimental data. During past years many theoretical models have been proposed to develop the equations of state for nanomaterials.

Singh and Gupta [30] have derived the integral form of isobaric EOS(IFEOS) in which they have considered the Gruneisen parameter as a temperature dependent function. This assumption in the equation of state describes the temperature dependence of thermo-elastic properties of nanomaterials more accurately and also predicts the results satisfactorily in low temperature range.

In the present work, we have used the Singh and Gupta’s and Murnaghan’s equation of state for some of the nanomaterials such as w-ZnO, r-ZnO, fullerene, 20nm Ni, Ag, Au, zirconia, AlN composites and Foresterite etc. for calculating thermal expansion, expansion coefficient and bulk modulus properties. The results achieved are found in good agreement with the experimental data.

1.4 Review of Literature

It is evident from the existing literature that during past years several experimental and phenomenological studies have been carried out to analyze the thermophysical properties of bulk materials under the effect of high temperature & high pressure. However, it is noted that the study of temperature and pressure dependent elastic properties of nanomaterials have been quite scare in past.

1.4.1 Experimental Studies of Nanomaterials:

Turi et al., [31] has measured the linear thermal expansion coefficient of porosity free electroplated nanocrystalline material in the temperature range between 40K and 500K. The isobaric specific heat of Ni is reported between 2.5%- 5% larger for the nano Ni than for the bulk Ni. However, for nanocrystalline – (Ni-Fe) the thermal expansion is observed in decreasing order above 350K which can be attributed to alloying effects.
Maniwa et al.,[32] have determined thermal expansion coefficient of single walled nanocarbon tube bundles as (-0.15±0.20)x10^{-5} (1/K) and (0.75±0.25)x10^{-5} (1/K) for the triangular lattice graphite by means of X – ray scattering in the range of 300 K - 950 K. The value for the intertube gap is (4.2±1.4) x10^{-5} (1/K), which is larger than 2.6x10^{-5} (1/K) in graphite. The result reveals that nanotube has more lattice anharmonicity than that of graphite.

Chen et al.,[33] have investigated the room temperature x-ray diffraction which yields zero pressure bulk modulus values of $K_{67}=238±3$ GPa and $K_{37}=172±3$ GPa for nanocrystalline γ-alumina ($\text{Al}_2\text{O}_3$) with particle size of 67 and 37 nm respectively. Under high pressure x-ray studies of 20 and 6 nm nanocrystal Al$_2$O$_3$, it is noted that the rigidity decreases with increasing the size of nanoparticle. A new phase is detected at pressure above 51 and 56 GPa for γ-Al$_2$O$_3$ of 67 and 37 nm respectively.

High temperature micro x-ray diffraction studies have been performed by Seeleboyina et al.,[6] on nanocrystalline and bulk samples of NiO, anatase TiO$_2$ and ZnO. The parameters of bulk and nano samples were determined from 475K-1417K for NiO, 300K-883K for TiO$_2$ and 300K-1426K for ZnO. The results obtained in this study show that the volume thermal expansion co-efficient of nanocrystalline NiO is higher than that of Bulk NiO crystal.

Mounet et al.,[7] studied the thermodynamic properties of diamond and graphite by using combination of density-functional total energy theory and density-functional perturbation theory. They found the good agreement of structural properties and phonon dispersions.

Kirtania et al.,[34] have recently analyzed the young’s modulus and co-efficient of thermal expansion (CTE) of single walled carbon nanotubes (SWCNT’s) and graphene sheets, using 3D finite element analysis (FEA). Both arm chair and zig-zag SWCNT’s have been analyzed and noted the following important observations:

- With the decrease in the size of the graphene sheets, the young’s modulus decreases.
• With the decrease in the wall thickness of nanotube the young’s modulus of both armchair and zig-zag nanotubes increases.
• With the decrease in tube diameter and the size of the graphene sheet, the coefficient of thermal expansion (CTE) of both armchair and zig-zag nanotubes and graphene sheet decreases uniformly.
• The coefficient of thermal expansion of the armchair nanotube is larger than that of the zig-zag nanotube measured along one axis of the nanotube.

Yoon et al.,[35] studied the coefficient of thermal expansion (CTE) and strain of twisted graphene with temperature dependent Raman spectroscopy. They found that TEC remains negative in the whole temperature range i.e., 200-400K and strain mismatch between graphene and its substrate.

1.4.2 Theoretical studies of nanomaterials:

Singh and Gupta [30] studied a straightforward method for calculating thermal expansion and its coefficient for minerals(MgO,CaO) under the effect of high temperature. It has been stated by them that the Anderson parameter ($\delta T$) should be considered as a function of temperature. They have reported a new form of equation of state to analyze the thermal expansion in minerals. The expression for the coefficient of thermal expansion is obtained by considering the Anderson parameter $\delta T$ as a parameter varying with temperature.

Jiang et al.,[36] have developed an analytical method to determine the coefficient of thermal expansion(CTE) for single wall carbon nanotubes(CNT’s). They reported that the thermal expansion coefficient remains negative up to the range of room temperature, however, CTE is found positive. It is reported that as the diameter of carbon nanotube is decreased the range of negative CTE shrunk. The CTE in axial direction of the CNT is more than that in the radial direction for armchair CNT’s. This indicates that the carbon nanotubes are extremely rigid in the axial direction.

Srivastava et al.,[37] have analyzed the pressure dependence of compression behavior of nanotube bundle and individual tube within the bundle of single wall
CNT’s. For this purpose, they have used Usual Tait’s Equation of State (UTE) to predict the change in unit cell volume as a function of pressure. They have also predicted the variation in bulk modulus and specific heat with pressure for nanotube. They concluded that the individual CNT is less compressible than the bundle of CNT’s.

Kandpal et al.,[38] have determined the thermal and compression properties of hcp iron (Fe) at high pressure and high temperature by considering the effect of phonon pressure in usual Tait’s equation of state.

Shanker et al., [39] explained the thermal expressivity which does not satisfy the infinite pressure behavior. The expressions for the volume dependence of the isothermal Anderson Gruneisen parameter have been found to be inadequate. Therefore, they explained the new formulation which reveals that $\delta_T$ infinity must be greater than zero and fits the approximate data on thermal expressivity for hcp iron to a wide range of pressure(0-360GPa).

Devlal et al., [40] have analyzed the thermo physical properties i.e., thermal expansion and bulk modulus of inert gas solids using Singh & Gupta equation of state (IFEOS). An excellent agreement has been found by them between the calculated values and experimental data.

Srivastava et al., [41] have analyzed thermal expansion coefficient and bulk modulus of fullerene $C_{60}$ at high temperatures. The $C_{60}$ structure consists of 60 carbon atoms that link together to form a hollow cage like structure by which they show the anomalous properties of bulk modulus and specific heat of the material as compared to bulk material. They obtained a good agreement of their results with experimental values.

Chandra et al., [42] have calculated the elastic properties such as volume thermal expansion, thermal expansivity and bulk modulus of different solids such as AgO,
AuO, NiO, MnO and alkali halides like NaCl and KCl by using the Singh and Gupta equation of state (IFEOS). The results show the decreasing trend of bulk modulus with increasing temperature according to the melting theory i.e. $K_T \rightarrow 0$ as $T \rightarrow T_m$.

Thermal properties of nanocrystalline materials differ from those of their bulk materials due to the large surface-volume ratio of nanomaterials. Chandra et al., [43] have studied the thermal properties of nanomaterials like n-ZnO, TiO$_2$ anatase, and n-NiO using the equation of state (IFEOS) under high temperatures. It is stated that the IFEOS successfully explains the thermo-elastic properties of nanomaterials.

Chandra et al., [44] have also studied the temperature dependent thermo-elastic properties of n-Ni and n-(Ni+ Fe) and calculated the thermal expansivity ($\alpha_T$), thermal expansion ($V/V_0$) and bulk modulus ($K_T$) by using the Singh and Gupta’s EOS. The results obtained by them for these materials predict the consistency with experimental data and also show the decreasing trend of bulk modulus with temperature as observed for bulk materials.

The knowledge of elasticity of minerals is useful for interpreting the structure and composition of the lower mantle of earth and also in seismic studies. The thermoelastic properties of minerals at high temperature have been analyzed by Upadhay et al., [45]. They modified the Kumar’s formulation considering the anharmonic effect in minerals above Debye temperature ($\theta_D$) and calculated the thermo-elastic properties of minerals like garnet and MgAl$_2$O$_4$ assuming $\delta_T$ as temperature independent.

Kumar et al., [46] studied the effect of temperature by an alternative method based on thermodynamics variables. They determined the effect of temperature on Zr, Ag, ZnO, NiO and Al composites by alternative method and reported a good agreement between theory and experimental.

Sharma et al., [47] have developed a new relationship for the temperature dependence of volume thermal expansion assuming that volume thermal expansion depends on the quadratic term of temperature and formulation was applied to
predict the values of thermal expansion coefficient of NaCl, KCl, MgO and CaO bulk crystals.

Singh et al.,[48] studied the thermal expansion of rock salt and wurzite phase of zinc oxide nanomaterials using different equation of state. It is stated by them that upto room temperature range the thermal expansion increases with slow rate in both the phases of zinc oxide while in high temperature range, however, the thermal expansion increases with high rate in rs-ZnO and slow rate in w-ZnO above room temperature.

Chandra et al., [49] also described the comparative analysis of thermal expansion, thermal expansivity and isothermal bulk modulus of zinc oxide nanomaterials (w-ZnO & rs-ZnO) under high temperature. They have used the equation of states described by various workers[50-59], however, the results obtained by them are not in good agreement with experimental data.

Kholiya et al., [60] have used the equation of state (EOS) to analyze the high pressure compression behavior of 3C-SiC, γ-Fe2O3, Rb3C60 and Zr0.1Ti0.9O2. They have assumed the pressure up to the quadratic terms of relative change in volume and density. The results obtained by them are found in good agreement with the experimental data and thus contradicts the Kumar’s equation in which the pressure is considered only up to the second term of relative change in volume.

Devlal et al., [61] have recently described the compression behavior of nanomaterials under high pressure by using the power series approach of the equation of state. The power series expansion of EOS is also capable of predicting the results successfully.

1.5 Motivation and Objectives

In view of the importance of nanomaterials and their applications in science & technology the investigation of the temperature and pressure dependence of thermo physical properties are, therefore, of current interest for those who are working in the fields of nanoscience and technology. Many experimental techniques are developed to synthesize and characterize the nanomaterials and thus provided the
Experimental data to initiate further theoretical studies. Therefore, several theoretical methods have been proposed during past decade to study the thermo-physical properties of nanomaterials under high temperature and high pressure. However, there is still scope to investigate the thermo-physical properties of those nanomaterials for which no appropriate model theory could provide the satisfactory results under the effect of high temperature and high pressure. There have been some drawbacks in theory-models used by the previous investigators. Motivated with this situation, we have used the theoretical model which yields the results close to the available experimental data and better than those obtained by the previous workers. The present research work deals with the theoretical study of those nanomaterials which are not explored extensively to analyze their thermo-elastic behavior under high temperature and high pressure.

To study the thermo-physical properties of nanomaterials under high temperature and high pressure two kinds of theoretical approaches can be used (i) Potential dependent model and (ii) Potential independent model. Since the potential dependent model consists of more parameters and complex computational work we have preferred to use the potential independent model which consists of only two or three input parameters. Potential independent model is a simple and straightforward model which requires less input parameters and yields better results.

The main objective of research work is to provide a simple and straightforward theoretical model to determine the thermal and elastic properties of nanomaterials under high temperature and high pressure. The model theory used in the present study is mathematically and thermodynamically consistent and explains the experimental results satisfactorily.

1.6 Research Methodology

The theoretical model has been employed to determine the temperature and pressure dependence of thermo physical properties like volume thermal expansion and bulk modulus of nanostructured crystals. The nanocrystals like 20nm-Ni, ZnO(wurzite, rocksalt), TiO₂, 11% AlN/Al, 39% AlN/Al, n-Ag n-Au, Graphene, n-Foresterite etc. are considered under the present investigation. The following procedure has been adopted in carrying out the entire research work:
After surveying the existing literature on the relevant research topic the selection is made for those nanomaterials for which the studies on anharmonic elastic properties are less explored.

The theoretical model based on Murnaghan equation of state has been first applied to determine the thermal expansion properties of some of the nanomaterials. The results so obtained for most of the nanocrystals were found not in good agreement with experimental data. The reason may be ascribed to the linear nature of expansion with temperature as considered in Murnaghan equation of state. However, the experimental results show the exponential nature of thermal expansion with temperature.

Another theoretical model which is based on temperature dependent equation of state that is the Singh and Gupta’s EOS which shows the exponential behavior of thermal expansion with temperature is employed in the present study to analyze the anharmonic elastic properties of nanocrystals.

The results achieved in the present investigation are compared with the available experimental data to test the validity and applicability of model theory used.

The research findings are discussed rigorously and concluded in last.