transitions are metallization of oxygen at ~ 96 GPa[10-11], metal to insulator transition in sodium at ~ 200 GPa [12], the hcp → three atom hexagonal (ω) → bcc (β) structural transformation in group IV transition metals Ti, Zr and Hf [13-16], the β to ω phase transition in tantalum and Zr-20%Nb alloy under transient loading to ~ 45 GPa and ~ 15 GPa, respectively [8-9, 17-18] etc. The discovery of such phase transformations in materials has added new dimensions to the understanding of behaviour of materials under high pressure. For example, the occurrence of hcp → ω → β structural phase transition in Ti, Zr and Hf under high pressure has been attributed to the transfer of electrons from filled s-band to the partially filled narrow d-bands and their distribution in various d-substates [19-21]. The knowledge of this structural sequence under pressure and its correlation with electron transfer from s-band to d-bands has added a new understanding in basic physics of transition metals and their alloys.

In addition to pressure induced phase transitions, the high pressure equation of state (EOS), e.g., isotherm, isentrope and Hugoniot also play important role in characterization of state of a material under pressure. The knowledge of EOS serves as vital input to the computer codes for the hydrodynamic simulations which are related to the wave propagation in geological media, reactor accidents, fission/fusion energy systems and in the analysis of many problems pertaining to geophysics, astrophysics and planetology [1, 2]. Similarly, the pressure dependent elastic constants of materials play important role in determining the mechanical failure strength and various physical quantities such as Debye temperature, sound velocity, Gruneisen parameter, etc. The ultrasonic technique [22] is commonly used to measure the elastic constants of materials at ambient pressure. The Brillouin scattering is another method of measuring elastic constants at ambient conditions as well as at high pressures of few GPa [23-24]. Further, the high pressure x-ray diffraction measurements in diamond anvil cell (DAC) under non hydrostatic stress conditions have been used to evaluate elastic constants up to few tens of GPa [25-26].
The mechanical failure strength of materials is of practical interest. The failure strength of a material is governed by the binding energy and the defects and dislocation present in the material. In a perfect solid, the failure strength is solely dependent on its binding energy; however, in case of a practical solid the failure strength strongly depends upon the defects and dislocations present in it. Beside the defects and dislocation, the failure strength of materials also depends on the rate at which the strains are applied [27-28]. In fact, it has been observed experimentally that the failure strength of a material measured under quasistatic loading differs significantly from that measured under high strain rate conditions [27-30]. This suggests that the knowledge of strength properties merely at quasistatic loading conditions is not sufficient when the suitability of a material for applications involving high strain rates has to be decided. For example, analysis of structural response of a material subjected to high strain rate loading conditions occurring during the propagation of seismic waves through geological media and the fracture and fragmentation at high velocity impact needs the failure strength at high strain rate as input. The strength measurements at high strain rate conditions are quite challenging and need special techniques for generation and measurements of high strain rates [31-34]. The well configured shock wave experiments which not only can generate the high compressive stresses but also the high tensile stresses at strain rates ranging from $10^4$/s to $10^9$/s are ideal tool for measurement of failure strength at high strain rates [35].

Besides the advancement in high pressure experimental techniques, a significant progress has been made in theoretical front also in last few decades [14-15, 17, 19, 36-37]. With the advent of much enhanced computational power, the \textit{ab-initio} theoretical methods based on density functional approach have been developed and employed for investigations of the phase transitions, equation of states, elastic properties, mechanical failure strength and pressure effect on melting point of materials [11, 14-15, 19, 36-40]. The present day theoretical methods are capable of not only reproducing the experimental results but also predicting the various new physical phenomena such as structural phase transitions, elastic and mechanical properties of the materials [37, 41-42]. For example, in calcium, the \textit{ab-initio} calculations performed by Oganov \textit{et al.} [37] predicted a $\beta$-tin type tetragonal structure (space group $I4_1/amd$) to be more favorable above 33 GPa. However,
the high pressure x-ray diffraction measurements by Mao et al. [43] reported a phase transition around 32 GPa and indexed this as rhombohedral structure (space group R-3m) at 300 K and orthorhombic structure (space group Cmmm) below 30 K. In view of this discrepancy between theory and experiment, Li et al. [44] repeated the high pressure experiment on this material and reported that the high pressure phase formed around 35 GPa is indeed a β-tin type tetragonal structure, consistent with theoretical prediction. In addition to predicting phase transitions, the ab-initio theoretical methods can be resorted as a tool to determine the ideal failure strength of materials under different deformation configurations and thus providing the information about the upper bound to the maximum stress that a given solid can withstand before failure under a particular deformation configuration. Further, the ab-initio theoretical methods have also been utilized to determine melting line of materials [39]. For example, molecular dynamic simulations or ab-initio static lattice calculations in conjunction with Lindemann melting criteria have been widely used to calculate the melting line and predict the melting of solids under shock loading [39, 45-46].

The present thesis deals with theoretical studies carried out on binary compounds LiH, LaN and MgO to understand the high pressure behavior of these materials. The theoretical work includes the analysis of structural stability, determination of 300 K isotherm, elastic constants and phonon spectra as a function of hydrostatic compression. All these compounds exist in rocksalt structure (B1) at ambient conditions and have attracted attention of researchers due to their technical as well as academic importance. For example, in hydride and deuteride of lithium, the major interest is due to their importance as thermo nuclear materials and the potential hydrogen storage compound. The LaN is among the transition metal mononitrides that exhibit unique physical properties such as high hardness, brittleness and melting point. Apart from this, the LaN encounters many problems related to stoichiometry [47]. The MgO, however, has been subject of extensive study due to its geophysical implications as it constitutes the major part of the lower mantle of the earth. In various theoretical studies carried out in past [48-64] on these isostructural materials have predicted the B1 to a simple cubic CsCl type (B2) structural phase transition under hydrostatic compression. For example, in LiH,
several theoretical studies predicted the B1 to B2 phase transition at the pressures ranging from 85 GPa to 660 GPa [48-54]. The experimental study performed up to ~ 250 GPa, however, shows no phase transition [65]. In LaN also, the theoretical studies [55-56] predicted the B1 to B2 phase transition and the transition pressure is put in the range of 25-27 GPa. The high pressure X-ray diffraction measurements carried out on this material in diamond anvil cell (DAC), however report the occurrence of a primitive tetragonal structure (B10, which can be viewed as distortion of B2 structure) with space group P4/nmm at ~ 22.8 GPa [66]. Likewise in MgO also, the theoretical investigations predict the B1 to B2 structural phase transition under hydrostatic compression with transition pressures ranging from 116 GPa to 1050 GPa [57-64]. The static compression experiment [67] carried out up to maximum pressure of ~ 227 does not show any phase transition in this material. It may be noted that the most of the theoretical predictions on phase transition in these materials are based on the analysis of structural stability of B1 and B2 structures only. In light of the experimentally observed occurrence of B10 structure in LaN, the B10 structure also becomes one of the plausible structure to be considered for structural stability analysis of such isostructured binary compounds. In spite of a large body of research work available on these materials there are still useful aspects of high pressure behavior which required to be investigated. For example, in LiH, studies related to the pressure dependent of elastic properties, ambient condition thermophysical properties, e.g., Gruneisen parameter, Debye temperature, and Hugoniot parameter were either limited or are not available. Similarly, in LaN, it is worth to investigate theoretically the existence of experimentally observed B10 structure and the cause for its occurrence. As far as MgO is concerned, no data are available on the mechanical stability of this material under uniaxial loading condition. Being a geophysically important material, the knowledge of its ideal strength for compression as well as for expansion under uniaxial loading condition will serve as an important input for simulation of wave propagations through geological media. The theoretical investigations on these binary compounds have been carried out mainly to address the above mentioned issues. Apart from the theoretical investigations on these compounds, the experimental work has been carried out in elemental solid copper also. The objective of the experimental work was to measure the tensile fracture strength of polycrystalline
copper subjected to high strain rate loading in shock wave experiments and compare it with that measured under quasistatic loading condition. The whole work presented in the thesis has been classified in six chapters.

The first chapter gives an introduction to the basic concepts of the high pressure, the different methods to generate high pressure in materials, the effect of high pressure in materials, various diagnostic techniques utilized to understand the behavior of materials under high pressure. Also, a brief description of modern DFT based *ab-initio* electronic band structure method used for understanding the material response under high pressures has also been provided along with illustrations on the predictive capability of these theoretical tools.

The Second chapter deals with the theoretical calculations carried out on LiH. In LiH, the objective was to perform the studies to determine the pressure dependent elastic properties, ambient condition thermophysical properties e.g. Gruneisen parameter, Debye temperature, and Hugoniot parameter. For this purpose, first the *ab-initio* calculations at 0 K have been performed to analyze structural stability by choosing the three structures namely B1, B10 and B2 as plausible structures. The 0 K calculations have been utilized to derive the 300 K isotherm after adding finite temperature corrections. The bulk modulus and its pressure derivative at zero pressure as well as at higher pressures have been determined from theoretical isotherm. Additional calculations have been performed to determine the shear elastic moduli as a function of hydrostatic compression. Our structural stability analysis suggests that the B1 phase will transforms to B2 phase at ~327 GPa. The theoretical equation of state derived from these calculations agrees well with the experimental data [68]. The zero pressure equilibrium volume, bulk modulus and its pressure derivative has been found to be 17.26 Å³/formula unit, 34.2 GPa, and 3.61 as compared to the experimental values [65] of 17.02 Å³/formula unit, 32.2 GPa, 3.53, respectively. Other physical parameters such as bulk sound velocity of 6.48 km/s, the shock parameter of 1.15, the Debye temperature of 828 K and the Gruneisen parameter of 1.30 agree well with the experimental data of 6.43 km/s [69], 1.16 [70], 1.2 [69] and 810 K[71], respectively. The elastic constants C_{11}, C_{12} and C_{44} of B1 phase at zero
pressure are calculated to be 77.0 GPa, 12.7 GPa and 48.2 GPa as compared to the experimental values of 74.06 GPa, 14.2 GPa and 48.43 GPa [69], respectively. The variation of elastic constants and elastic anisotropy with pressure was determined and the polycrystalline elastic moduli have also been calculated. Calculations are further extended to determine the phonon spectra of B1 phase of LiH as a function of compression up to 120 GPa [72]. The phonon spectrum calculated at zero pressure is in agrees reasonably with the experimentally measured data [65, 73-74]. The X-point phonon frequencies calculated at various pressures up to maximum of 120 GPa have been compared with the available experimental data [65].

The third chapter of the thesis is devoted to the analysis of structural stability, and determination of equation of state and elastic properties as a function of hydrostatic compression for MgO, a geophysically important material. To analyze the structural stability, the total energy calculations have been carried out on the B1, B10 and B2 structure of MgO and enthalpy has been determined as a function of pressure. The comparison of enthalpies of B1, B10 and B2 phases suggests the B1 to B2 structural transition at \( \sim 535 \) GPa, in line with the available theoretical findings [57-64]. The 0 K energy-volume relation in conjunction with thermal corrections has been utilized to derive the isotherm, isentrope and Hugoniot of this material. A good agreement has been found between the theoretically determined isotherm, isentrope and Hugoniot with the experimental data [75-80]. The theoretical investigations have been further extended beyond the hydrostatic conditions and the elastic moduli of MgO single crystal have been determined as a function of strain for uniaxial loading along [001] crystallographic direction under two deformation configurations “uniaxial stress condition” and “uniaxial strain conditions”, respectively. The ideal failure strengths for compression and expansion under these two deformation configurations have been determined by examining the elastic stability conditions throughout the deformation path. It may be noted that the uniaxial stress condition is commonly encountered in quasistatic experiments, however, the uniaxial strain condition exists in high strain rate experiments e.g. uniaxial compression and expansion generated in shock wave experiments. The determination of elastic moduli as a function of [001] strain and examination of the elastic stability condition at each strain suggested that for [001] uniaxial expansion, the
MgO single crystal will fail due to vanishing of tensile modulus, whereas it will fail due to shear instability under uniaxial compressive loading. The ideal compressive strength and ideal tensile strength for compressive and tensile loading along [001] direction under uniaxial strain condition are determined to be \( \sim -283 \) GPa and \( \sim 20 \) GPa, respectively; the same under uniaxial stress condition are evaluated to be \( \sim -115 \) GPa and \( \sim 11 \) GPa, respectively. These findings suggest that the ideal compressive and tensile strength of MgO single crystal is higher for uniaxial strain condition than that for the uniaxial stress condition.

The fourth chapter presents the theoretical high pressure investigations on LaN. Unlike the LiH and MgO, this material is experimentally reported [66] to undergo pressure induced phase transition from B1 phase (high symmetry cubic structure) to a tetragonal (B10) phase (low symmetry structure named as HP-LaN by authors) at \( \sim 22.8 \) GPa. Whereas theoretical studies [55-56] prior to this experimental work have not included the tetragonal structure in their calculations and predicted the B1 to B2 phase transition in this material. We analyzed the structural stability of this material under hydrostatic compression by performing total energy calculations on B1, B2 and B10 (HP-LaN) structures. The present theoretical calculations suggest the B1 to HP-LaN transition at \( \sim 19 \) GPa as compared to the experimental value of 22.8 GPa [66]. Further, we predict that the HP-LaN phase transforms to B2 phase at \( \sim 169 \) GPa. While the B1 \( \rightarrow \) HP-LaN transition is of first order in nature with 9% volume discontinuity, the HP-LaN \( \rightarrow \) B2 transition is of second order in nature. To understand the cause for the existence of lower symmetry HP-LaN phase (a distortion of the B2 structure) prior to the stabilization B2 structure at higher pressures, we have analyzed the band structures of HP-LaN and B2 phase. Our analysis suggests that the low symmetry HP-LaN phase could be stabilized at lower pressure due to symmetry breaking lowering of total energy.

The fifth chapter reports the experimental measurements of the tensile fracture strength and yield strength of polycrystalline copper subjected to uniaxial loading at strain rates of \( \sim 10^4/s \), generated in shock wave experiments carried out using single stage gas gun existing in our laboratory at BARC [81]. Additionally, the sample retrieved from
peak shock loading of ~ 10 GPa are analyzed using nanoindentation technique to look for shock induced changes in its hardness and Young’s elastic modulus. The yield strength and spall strength of 0.14 GPa and 1.32 GPa, measured at strain rates ~ 10⁴/s from free surface velocity history measured using VISAR are higher by a factor of ~ 2.0 and 6, respectively, than the quasi static loading values. Further, the nanohardness and the Young’s modulus have been determined to be 1.43 GPa and 239 GPa, respectively from the indentation method as compared to 1.21 GPa and 185 GPa for as-received sample. This signifies that the hardness and Young’s modulus increases upon shock treatment on material.

The thesis will be concluded in the sixth chapter giving a discussion and summary of the overall work presented followed by further research scope open in the present field.

References


Investigations on pressure induced B1-B10-B2 phase transitions in binary systems
LaN, LiH and MgO

(SYNOPSIS)

Research on material properties under high pressure has attracted attention of scientific community since four decades and there are some fascinating results which enriches the basic and applied sciences [1-5]. Pressure is a thermodynamical variable which can be tuned in precise way to induce changes in materials properties similar to those brought by the application of temperature. The application of pressure can cause the reduction in volume of condensed matter by more than a factor of two and thus revealing many interesting changes in properties of materials under compression. The high pressures in the materials are generated either by static compression methods or by dynamic compression (shock compression) methods. The two methods of high pressure generation differ widely. In the static compression technique [4], material is squeezed slowly; hence, temperature inside the sample during the experiment remains constant i.e. the static compression is an isothermal process. To some extent, in static method one can compress the material hydrostatically by selecting a suitable (fluid or gas) pressure transmitting medium surrounding the sample [4,6]. In shock loading methods, on the other hand, materials are compressed uniaxially with very high rate of pressurization (rise times ~ few tens of nanoseconds), and the temperature and entropy of the materials always increase. Under static compression, the duration of the pressure on the material can be as long as we desire, however, in shock compression the duration of pressure pulse is very small (of order of few microseconds) depending upon the dimensions of the sample. Unlike the hydrostatic compression, the shock loading is always accompanied by the shear stresses which may induce phase transitions that are not observed under hydrostatic loading. For example, in tantalum (Ta) the body centered cubic (β) phase is found to be stable under hydrostatic compression up to 170 GPa whereas under shock loading it transforms to ω phase at ~ 45 GPa [7-9].

Phase transitions are examples of the striking changes that can be brought by application of pressure in materials. Some of the interesting pressure induced phase