Chapter I

Introduction and Motivation

Pressure and temperature are the two commonly employed thermodynamic variables to vary the interatomic distances in matter. In respect of the solid state these offer the cleanest means to manipulate the bond length, bond angle and even the nature of the bonding compared to chemical means. Application of pressure and temperature separately or simultaneously can induce a variety of phase transitions (structural, electronic, magnetic-nonmagnetic, metal-insulator, normal-superconductor) and enable novel chemistry. This thesis provides example of both aspects. The first part illustrates the fascinating role that simultaneous application of pressure and temperature can play in inducing chemical bond formation between seemingly unreactive elements belonging to Group IV of the periodic table. The second part describes observation of interesting structural and dynamical behavior induced by high pressure in a class of layered mixed halides of lead, known as “Matlockites”. This introductory chapter starts with a section discussing in general terms the effect of pressure and temperature on materials (Sec.1.1). High pressure structural phase transitions of group IV elements and their structural stability studies reported in the literature are discussed next in the context of the present thesis problems with focus on X-ray diffraction and Raman spectroscopy (Sec.1.2&1.3). Motivation for studying binary systems constituted of pairs of Group-IV elements is discussed in detail in the section on IV-IV compounds (Sec.1.4). The relevance of using Laser Heated Diamond Anvil Cell technique (LHDAC) for attempting synthesis of novel
1.1 Effect of Pressure and Temperature on Materials

Pressure, temperature and chemical composition are the three important thermodynamic variables which determine the stability and reactions of molecules and solids [1]. By manipulating temperature and composition, a rich number of structures and compounds can be obtained. Compared to the other two variables “high pressure” has an important place in condensed matter physics. Pressure is a special case of generalized stress, by which one can change the volume of a system or the average particle density [2]. The unit of pressure used in this thesis is Pascal (Pa), 1 Pa =1 N/m² and 1 bar =10⁶ dynes/cm² =10⁵ Pa, 1 GPa =10⁶ Pa =10 kbar. The pressure of the order of tens to hundreds of atmosphere shows significant effects on organic and inorganic chemistry. But these pressures are very low to cause any substantial changes in chemical bonding or crystal packing in condensed matter system [1]. Pressurizing materials to ~kbars and above offers a route to "breaking down" the electronic structure of the atoms and to the possibility of having entirely different bulk properties, as was first demonstrated extensively by Percy Bridgman [3]. At pressure of ~100 GPa, the energy density achieved on compression is comparable to the chemical bond energies (few electron volts) [4]. Using pressure, much more extreme states of condensed matter can be achieved as compared to the effect of temperature. As pressure causes increase the coordination number—which is related to the changes in electron hybridization—it can
induce chemical reactions that do not occur at normal conditions and also it can speed up or slow down a chemical reaction (change in chemical reactivity) [2]. The heating of the sample which is squeezed inside a high pressure apparatus can provide kinetics required for the reacting species to overcome the activation barriers and thereby react to form novel compounds [5]. In this way we can synthesize materials with exotic mechanical, optical or electronic properties.

1.2 High Pressure Behavior of Group IV Elements

The first part of the thesis describes exploration of formation of inter-group alloys or compounds involving the Group-IV elements employing the HP-HT synthesis route. According to the Hume-Rothery conditions of alloy formation, one of the conditions is the similarity of structure of the elements involved in the alloy formation. So for the HP-HT synthesis of binary alloys, it is very essential to know the high pressure behavior of the elements of interest in the required pressure range. High-pressure behavior of the elements involving the group-IV; C, Si, Ge, Sn and Pb has been the subject of many experimental and theoretical investigations [6]. These elements undergo a series of pressure induced structural phase transitions and high pressure behavior of these systems is interesting from the view point of basic research. The rest of this section gives a brief overview of the pressure induced behavior of the group-IV elements.

1.2.1 Silicon & Germanium

The properties of both Ge and Si under high pressures are almost similar. Si and Ge are indirect band-gap semiconductors and crystallize in cubic diamond structure [7]. Around
10 GPa, both Ge and Si undergo a pressure induced structural phase transition from the cubic diamond structure to the β-Sn structure. High pressure β-Sn phase of Ge has a tetragonal structure. The crystal structure of β-Sn is shown in Fig.1.1. On further applying pressure, the β-Sn phase transforms into a simple hexagonal (sh) phase via an intermediate body centered orthorhombic structure at ~13.2(3) GPa with space group Imma [8-10]. Like Si, the stability range of the Imma phase of Ge is observed in the pressure range ~75 to ~85 GPa [10-12]. High pressure studies on Ge using nanocrystalline material reveal that the transition from β-Sn to Imma phase is second order phase transition whereas that of Imma to sh phase is of first order with the corresponding transition pressures at ~66 GPa and ~90 GPa respectively [12].

![Fig.1.1. Crystal structure of β-Sn. The lattice information is taken from crystallography open data base. The space group and the atomic positions of Sn atoms are I41/amd and Sn (0 0 0) respectively.](image)

For Ge at ~135 GPa, another high pressure phase with space group Cmca with 16 atoms in the unit cell are observed [13-16]. This structure does not occur in any elemental solid at ambient conditions. The Cmca phase of Ge is stable in the pressure
range of 91-155 GPa [17]. Angle-dispersive x-ray diffraction studies of Ge by Takemura et al confirms that the orthorhombic phase exists at pressures between about 100 and 170 GPa [18]. Full profile Rietveld refinement shows that this phase is an orthorhombic phase with space group \textit{Cmca} (Z=16) and atom position parameters very similar to those of Si-VI stable near 42 GPa [18]. The structure of \textit{Cmca} phase of Ge is shown in Fig.1.2. On further applying pressure to the Si and Ge systems, the \textit{Cmca} structure undergoes a phase transition to the hexagonal-close-packed (hcp) structure. This transition is seen in Si around 41 GPa whereas that of Ge seen at much higher pressure of 160-180 GPa [18-19]. The evidence for the existence of \textit{Cmca} phase of Si was observed for the first time by Olijnyk et al [16, 19-20]. The hcp structure of Si undergoes another phase transition to the face centered cubic (fcc) structure at about 87 GPa and this structure remains stable.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{fig1_2.png}
\caption{The crystal structure of \textit{Cmca} phase of Ge. Orange red and dark green colors indicate the positions of the of Ge1 and Ge2 atoms respectively. The atomic sites of Ge1 and Ge2 are 8(f):(0.221 0.000 0.000) and 8(d):(0 0.1721 0.3138) respectively.}
\end{figure}
up to 248 GPa [21]. But the hcp structure of Ge does not undergo further phase transition up to 190 GPa [18].

In summary, the sequence of pressure induced structural phase transitions observed in Si and Ge systems are: cubic diamond (cd) → β-Sn → Imma → simple hexagonal (sh) → Cmca → hcp. In addition to this, a further phase transition observed in Si is from hcp → fcc at ~87 GPa [7]. This sequence of phase transitions indicates a monotonic increase in coordination number of the high pressure phases on increasing pressure.

When pressure is released from high pressure phase of Si and Ge systems, at room temperature, they do not directly recover to the ambient cd phase; instead they form several other high denser tetrahedral phases. If the β-Sn phase of Si is decompressed slowly, at about 10 GPa it forms rhombohedra r8 phase and also form bc8 phase at about 2 GPa [22]. This transition is found to be perfectly reversible. At normal conditions, the bc8 phase remains as a metastable phase [23]. The slow decompression of Ge β-Sn phase leads to the tetragonal st12 phase and this phase persists as metastable phase at ambient pressure [24-26]. If the pressure of the Ge sample is released rapidly, then another new phase, bc8 is formed. This phase is similar to the phase observed in Si and unlike Si this phase does not persist for a long period of time [27-28]. So when a synthesis experiment is performed with these elements, depending on the P-T conditions these phases also have to be considered. The knowledge of these phases is essential to confirm whether the phase formed is a new compound or high pressure phases of constituent elements.

1.2.2 Carbon

Antoine Lavoisier in 1792 and Smithson Tenet in 1797 demonstrated that
diamond and graphite are allotropic forms of carbon. Since then man has been interested in converting abundant graphite on the earth into the much rarer diamond [29]. Graphite is one of the pure forms of carbon and stable under normal conditions. It is built from hexagonal planes of carbon atoms stacked in an ABAB manner. The arrangement of atoms in crystals of graphite consists of parallel stacking of layers containing carbon atoms in the hexagonal rings. In graphite lattice, the carbon atoms are bonded by strong covalent bonds whereas the adjacent planes are bonded by much weaker bonds. Hence the interlayer distance (3.35 Å) of graphite is higher than that of the in-plane nearest-neighbor distance (1.42 Å). This strong anisotropy of the bonding is reflected in the elastic and vibrational properties of graphite [30]. The nearest neighbors within a layer in the graphite has stiff sp\(^2\) covalent bonding whereas the adjacent layers are bonded by weak Van der Waals bonding which makes the graphite more compressible than diamond and also functions as a very good solid lubricant [7].

The first diamond synthesis was carried out at the General Electric Company based on the idea that diamonds can be crystallized from troilite, a rare iron sulfide mineral with the formula of FeS [29]. In this experiment, “Belt” apparatus was used to achieve high pressure. At 1650°C and 95,000 atmospheres, carbon atoms obtained from graphite or metallic carbides in the reaction mixture migrate through FeS solvent and precipitate as diamond [29]. The refractive index of the man made diamond was in the range 2.4-2.5 [31]. Yusa et al were successful in synthesizing diamond by converting graphite to diamond by heating the sample in a diamond anvil cell at ~13.9 GPa and around 3000 K [32]. Due to very large activation energy, the graphite to diamond transition need high pressure and high temperature of the order of (~ 5-9 GPa and 1200-2800 K) in the presence of transition-
metal catalysts. The diamond phase of carbon is insulator with indirect band gap whereas graphite is a zero gap semimetal. The high hardness of diamond is due to its sp\(^3\) bonding. Graphene is an allotrope of carbon. It is a carbon sheet having a single or few atomic layer thicknesses which has unusual physical properties and is the fundamental building block of carbon materials including graphite. The graphite is made up of stacks of sp\(^2\) bonded planar graphene sheets [33]. Raman spectra of all carbons have common features in the range 800-2000 cm\(^{-1}\) [34, 35, 36]. Carbon has a doubly degenerate, E\(_{2g}\) phonon mode at \(\sim1580\) cm\(^{-1}\) (G peak) at the centre of the Brillouin zone. Another mode called breathing mode of sp\(^2\) ring (D peak) is at \(\sim1350\) cm\(^{-1}\), which requires a defect for its activation. In addition to this, graphite has a rigid layer shear mode at \(\sim42\) cm\(^{-1}\). High pressure study of graphite shows the rigid-layer shear mode E\(_{2g}(1)\) at \(\sim44\) cm\(^{-1}\) and the in-plane mode E\(_{2g}(2)\) at \(\sim1579\) cm\(^{-1}\) increase sublinearly with pressure. High pressure study of graphene shows that the properties of graphene under compression are intrinsically similar to graphite [37].

1.2.3 Tin

Below 286 K and at normal pressure, tin transforms from the cubic diamond structure (\(\alpha\)-Sn) into the metallic \(\beta\)-tin structure. The \(\alpha \rightarrow \beta\) transition is accompanied by a volume collapse of \(\sim20\) %. When the sample is pressurized, around 9.5 GPa, the \(\beta\)-tin structure is transformed to the body-centered tetragonal structure [38]. On further pressurizing the sample, at around 40 GPa, the body centered tetragonal structure is transformed into body-centered cubic structure [39]. High pressure study of Sn has been studied up to a maximum pressure of \(\sim120\) GPa and do not observe any new phase at
1.2.4 Lead

At room temperature lead crystallizes in the face-centered-cubic structure and at ~13 GPa, it transforms to the hexagonal-close-packed structure [41]. On further increasing the pressure, at ~110 GPa, a further transition from the hcp structure to bcc structure is observed [42]. In both of the above phase transitions, the change in volume is very small and there is a large region of co-existence of phases.

1.3 Pressure Dependence of Phonon Modes of Group IV Elements

Since Si and Ge are semiconductors and also these adopt different crystal structures at high pressure, it is very interesting to study the pressure dependence of phonon modes of these elements. Most of the studies on these materials have been aimed at finding the mode Grüneisen parameter which gives the information about the lattice-dynamical properties (anharmonicity) of the materials. The first-order Raman spectra of these materials are obtained by the scattering of long-wavelength optical phonons. In polar semiconductors with different atoms in the unit cell, a study of the splitting of longitudinal optical (LO) and the transverse optical (TO) phonon modes give information of the dependence of their ionicity on volume [19]. The first order optical vibrational modes of lattices of diamond structure are Raman active, but not infrared active [43]. The first order Raman spectra of Si and Ge are reported at ~520.2±0.5 cm⁻¹ and ~300.7±0.5 cm⁻¹ respectively [44]. Both Ge and Si undergo phase transformations at ~10 GPa and ~12 GPa respectively [43, 19]. A group-theoretical analysis of lattice vibrations in the β-tin lattice shows that at the Γ point of the Brillouin zone the optical modes have
one LO phonon mode and a doubly degenerate TO mode. Both of the above modes are Raman active. The Raman spectra of Si in its high pressure $\beta$-Sn phase shows the frequency of the TO mode increases with pressure whereas that of LO mode decreases and broadens with pressure. In Ge, the frequency of TO mode increases with pressure similar to Si whereas LO mode initially increases with pressure and reaches a maximum value at $\sim 50$ GPa [45].

Graphite is built from hexagonal planes of carbon atoms and it contains four atoms in the unit cell with space group $P63/mmc$ ($D_{6h}$) [46]. The irreducible representations of the zone-center optic modes can be decomposed into the following [47-48]

$$\Gamma = A_{2u} + 2B_{2g} + E_{1u} + 2E_{2g}$$

where the $A_{2u}$ and $E_{1u}$ modes are IR active modes, observed at $\sim 867$ and $\sim 1588$ cm$^{-1}$ respectively. The $E_{2g}$ modes are Raman active, which are observed at $\sim 42$ and $\sim 1581$ cm$^{-1}$. The $B_{2g}$ modes are optically inactive. One of these modes has been reported at $\sim 127$ cm$^{-1}$ and the other nearer to $A_{2u}$ using neutron scattering experiments. The Ramp-Wave Compression (RWC) techniques show that the diamond phase of carbon is stable and strong up to 800 GPa [50]. In the case of Ge, the TO mode shifts to higher frequencies with increasing pressure, whereas the LO mode frequency initially increases slightly with pressure and reach a maximum at around 50 GPa [45].

The Raman study of tin shows that at ambient pressure two phonon modes at $\sim 42.5$ cm$^{-1}$ and $\sim 126.6$ cm$^{-1}$ [49]. Both of the above modes are blue shifted with pressure and the initial slope of TO phonon mode is five times that of LO phonon mode [49]. At
room temperature tin has tetragonal (\(\beta\)-tin) structure with 2 atoms in the unit cell and has three acoustical and three optical branches [49]. Group theoretical analysis carried out by Chen shows that at the \(\Gamma\) point of the Brillouin zone, the optical modes consist of one LO branch and a doubly degenerate TO branch at higher frequencies [51]. The phonon dispersion relations for acoustical and the optical branches for \(\beta\)-Sn at 110 K was studied by Rowe using inelastic neutron scattering experiments [52]. In this study, he reported the phonon dispersion relation of symmetry and some nonsymmetry branches with wave vectors along the [0, 0, \(\zeta\)], [1,0,\(\zeta\)], [\(\zeta\),0,0] and [\(\zeta\), \(\zeta\), 0] (\(\Lambda\), \(V\), \(\Sigma\) and \(\Delta\)) directions. The effect of pressure on \(\Gamma\) (TO) phonon mode is affected much more than that of \(\Gamma\) (LO). In the case of lead, it doesn’t have any Raman active modes.

1.4 IV-IV Systems

The intra group-IV semiconductor alloys formed from Carbon, Silicon, Germanium and Tin have immense potential for applications in the next generation of electronic and photonic devices [53-54]. The alloys and compounds of Si-Ge, Si-Sn and Ge-Sn are expected to be having unique optoelectronic properties for usage in quantum-well inter-subband technology [55]. The band gap and strain engineering of Si/SiGe heterostructures can be possible using silicon technology to improve the microelectronic device performance. The Ge\(_{1-x}\)Sn\(_x\) alloys with diamond cubic structures are very important in the optoelectronic industry due to the theoretical prediction and the experimental evidence for the existence of tunable direct band gap [56]. The band structure calculations of germanium carbide (Ge-C) predict its properties are similar to Si-C, and can be used in electronic and optoelectronic applications. Also it has a wide
band gap, high bulk modulus and its percentage of covalency is comparable to Si-C [57]. The high pressure study on Si-C using ab initio pseudopotential calculation predicts the zinc-blende structure of Si-C transforms into the rocksalt phase at hydrostatic pressure of 66±5 GPa [58]. This section describes some of the important IV-IV systems and highlights the novel techniques adopted to form them.

1.4.1 Si-Ge System

Si-Ge is a technologically important alloy due to its range of applications in Optoelectronic devices including mobile phones. Since the development of Si-Ge has improved the performance of silicon transistors using the developments of the Si-Ge heterstructure bipolar transistor (HBT) and strained-Si complementary metal oxide semiconductor (CMOS) technologies [53]. It is expected that in future all silicon based transistors, electronic and optoelectronic devices might be having some Si-Ge material [53]. At ambient pressure, the Si-Ge system forms a complete solid solution and is used in heterojunction bipolar devices [59]. Using Si technology, the band-gap and strain of Si/SiGe heterostructures can be engineered [53]. The Si$_{1-x}$Ge$_x$ alloy crystallizes in cubic diamond structure with the Si and Ge atoms distributed randomly [60]. Both Ge and Sn systems are indirect band gap semiconductors. The atomic radii ratio of Ge and Si is below 15 %, both of them have same crystal structures at ambient pressure. Hence they easily form a complete Ge-Si solid solution [61]. McGaff et al reported the high pressure synthesis of Ge-Si solid solution in β-Sn structure [60]. In this study they recovered Ge-Si alloy from the HP-HT conditions of ~15 GPa and ~1500 K. The atomic and electronic properties of the recovered Ge-Si phase were different from those of cubic Ge-
Si alloy.

1.4.2 Si-C System

Silicon carbide (Si-C) is a wide band-gap semiconductor and it has electronic, optoelectronic, optical, thermal and mechanical applications in high-power and high temperature devices. Due to its unique mechanical, chemical, electrical and thermal properties, it is used in various technological applications. Under normal conditions, it adopts many stable and long-range ordered modifications (polytypes) [62]. Due to its outstanding mechanical properties, Si-C is used as an abrasive. The bulk modulus of Si-C is quite high (321.9 GPa) [63].

A considerable number of research work has been reported to find the suitable experimental conditions to achieve high quality c-SiC films to grow pseudomorphically on silicon surfaces [64]. For that, several carbon sources have been reported to grow silicon carbide films on Si. For the synthesis of c-SiC films, the substrate temperature plays a crucial role to incorporate carbon atoms in the silicon matrix. The c-SiC films can be synthesized by the exposure of a hot silicon substrate at the temperature range between 600 and 900°C to acetylene, ethylene, graphite and C₆₀ [65].

1.4.3 Ge-Sn System

Ge-Sn alloy is expected to have more potential applications than Si-Ge due to the prediction of direct band gap formation and lattice matching with Si [66-67]. The thermodynamic solubility of Sn in Ge is less than 0.5 at %, while that of Ge in Sn is zero [68]. Thin films of Ge₁₋ₓSnₓ alloy have been synthesized using chemical vapor
deposition (CVD) methods [69], pulsed UV laser annealing using excimer lasers etc [70]. The electronic theory based on pseudo potentials and the virtual crystal approximation predicts the formation of a bulk Ge-Sn solid solution under high pressure [71]. A first principle calculation based on density functional theory predicts the stability of Ge-Sn alloy in the zinc-blende phase up to 9 GPa [72]. However, the bulk synthesis of Ge-Sn has not been realized yet. The challenges involved in the bulk synthesis of Ge-Sn are large lattice mismatch, low solubility, different crystal structures and different electronegativities of Ge and Sn at ambient pressure. Recently, bulk synthesis of a Ge$_{0.9}$Sn$_{0.1}$ system has been reported using piston-cylinder apparatus or multi-anvil press at ~2000 K and in a narrow pressure range of 9-10 GPa. The structural phase transitions in both Ge (diamond-type to β-Sn-type) and Sn (β-Sn to bct-Sn) in this narrow pressure range are deemed important to bring about the reaction on account of optimal match of the atomic radii and electronic structures [73-74]. In the section 1.5, we discuss the requirement of fast quenching of the sample laser heated at predetermined pressure using the laser Heated Diamond Anvil Cell technique (LHDAC).

1.4.4 Ge-C System

The Ge-C and Sn-C alloy systems formed as thin films on Si substrate seem to be a wide range of tunable band gap energies extending from the infrared to the near ultraviolet region of the electromagnetic spectrum. Since the elemental constituents forming the Ge-C, Sn-C, Ge-Sn etc alloys are immiscible under normal P and T conditions, the epitaxial stabilization of these alloys were attempted by various workers. The structural, electronic and optical properties of Ge-C epitaxial films have been
investigated both experimentally and theoretically [75-76]. Total energy calculations at 0 K based on pseudo potential approximation done by Sankey et al shows that Ge-C is unstable towards bond formation up to ~15 GPa [77]. But in this calculation, the energy released during the phase transition from cubic diamond to β-Sn structure at around 9 GPa was not taken into account. In addition, if the above energy released during phase transition was included in the total energy of the system, then it would change the transition pressure value. Also, the calculations based on the density functional theory shows that there is a propensity towards stable Ge-C alloy formation only above ~25 GPa and in this calculation also, the energy released during the phase transition from cubic diamond to β-Sn at around 9 GPa is not taken into account [75]. The bulk synthesis of these completely immiscible systems is not successful using conventional methods.

1.5 Relevance of LHDAC Technique for the High Pressure-High Temperature Synthesis of IV-IV Systems

Laser-heated diamond anvil cell technique (LHDAC) is a unique method to attain ultrahigh static pressure and temperature conditions of P >200 GPa and T ~12000 K [78-80]. After the invention of LHDAC in late 1960s, it has been coupled with various experimental techniques such as in situ Synchrotron x-ray diffraction [80], X-ray spectroscopy [81], optical spectroscopy [78] and visual observations [82-83]. Using this technique, a variety of materials such as silicates, oxides, metals and metal alloys have been subjected to extreme pressures and temperatures. The equations of state, crystal structures and structural dynamics of these materials have been examined by in situ x-ray diffraction and Raman spectroscopy. This technique is also used to synthesize novel and
super-hard materials under high pressure and temperature conditions. The laser heating of the sample squeezed between the diamond anvils in a DAC is used to provide the kinetics necessary for the reactant species to overcome the activation barriers and react to form novel materials which may have exotic properties [5].

Except “Si-C”, the formation of other compounds from group IV elements is not successful by the conventional equilibrium methods. Non-equilibrium techniques like pulsed laser ablation, chemical vapor deposition, molecular beam epitaxy and sputtering were employed to synthesize thin films of binary alloys from group IV elements. The difficulty in the bulk synthesizing of IV-IV compounds are due to their small electronegativity difference, low and positive formation enthalpy, large difference between the melting points of the elements (For example, Ge (1211 K) and Sn (505.1 K)), surface segregation of one of the elemental components due to low surface energy and difference in their structures at ambient P and T [63, 84-85]. Fast heating and quenching of samples at high pressure, mimicking nearly non-equilibrium conditions, can be achieved by employing a high power infrared laser focused on to the sample in a DAC [86]. The LHDAC technique has not yet been exploited to explore formation of the IV-IV systems. Apart from easily arriving at the required P-T conditions, the technique also paves way for in situ characterization vide XRD or optical spectroscopy. For instance Raman spectroscopy of laser heated mixtures of IV-IV elements at high pressure can instantaneously reveal signatures of new bond formations, if any.

1.6 Matlockite Compounds

The second part of the thesis describes the role of pressure in the structural behavior of layered matlockite compounds. The experimental study of the effect of
pressure on the structural properties of layered ionic compounds has been extensively investigated due to their importance in geophysics, and also to understand how the high pressure affects weak and strong bonds in condensed matter [87]. Ionic layered compounds of the form MFX, where M is a divalent metallic cation (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$ or Eu$^{2+}$) and X =Cl$^-$, Br$^-$ or I$^-$, crystallize in tetragonal structure with space group $P4/nmm$ [88]. A typical unit cell of MFX has two formula units in which the arrangement of atomic layers perpendicular to the c-axis is in the following sequence

$$F^- - M^{2+} - X^- - X^- - M^{2+} - F^-$$

*Fig.1.3.* Unit cell of PbFCl compound. The spheres with the labels F$^-$, Pb$^{2+}$ and Cl$^-$ represent the type of ions. The lattice information is taken from crystallography open data base. Ionic positions are Pb (0 0.5 0.2); F (0 0 0) and Cl (0 0.5 0.65).

The unit cell of PbFCl compound (matlockite) is shown in Fig.1.6. These materials have interesting properties such as photoconductivity [89], photoluminescence [90] and aniso-
tropic ionic conductivity [91] and find application in various fields. For example, BaFBr doped with Eu$^{2+}$ (BaFBr:Eu$^{2+}$) has been successfully applied for detecting X-rays as Imaging phosphors due to the photo stimulated luminescence property [92]. Similarly BaFCl:Sm$^{2+}$ is used as a pressure sensor in the high pressure experiments [93]. Though the bonding in the solid is primarily ionic, the binding is weak between the two Cl$^-$ layers. The apparent binding between the Cl$^-$ layers stems from the large polarizability of Cl$^-$ ions and Coulombic attraction exerted on the Cl$^-$ ions in one layer by the M$^{2+}$ ions in the second nearest neighbor layer. These therefore have anisotropic bonding scheme which manifests in their physical properties such as compressibility, conductivity and optical properties.

1.7 Structural Stability of Matlockite Compounds under High Pressure

1.7.1 HPXRD Studies

High pressure structural stability of the layered matlockite compounds BaFCl and BaFBr have been reported up to a maximum pressure of ~35 and ~60 GPa respectively [94-95]. These systems undergo a series of symmetry lowering structural transitions: tetragonal $\rightarrow$ orthorhombic $\rightarrow$ monoclinic and have been attributed to a gradual anisotropic distortion of the charge distribution in the planes perpendicular to the stacking direction [94-96]. In BaFCl system at around 10.8 GPa, the starting tetragonal phase is transformed to the orthorhombic phase and on further applying pressure, at around 21 GPa, the orthorhombic phase is transformed into monoclinic phase with space group $P2_1/m$. Similarly, the BaFBr compound undergoes a pressure induced structural transition from starting tetragonal phase to monoclinic phase via an intermediate
orthorhombic phase at around 12 and 27 GPa respectively. The phase transition reported is sluggish in nature probably due to the small Gibb’s free energy differences between the parent and daughter phases [97]. Observation of co-existence of parent and high pressure phases are reported in these compounds [95, 97]. High pressure study of BaFI compound has been reported up to a maximum pressure of ~102 GPa [95]. The study shows that like other matlockite compounds, this compound also undergoes a similar structural phase transitions at around 2.4 and 55 GPa respectively [95]. The reason for this sequence of phase transitions in these compounds is explained below. In MFX (M=Ba and X=Cl, Br or I) compounds, the adjacent X\(^-\) ion layers are bonded by weak ionic bonding. There exists an attraction of the M\(^{2+}\) ions with both X\(^-\) and F\(^-\) ions. Similarly there exists repulsion between the adjacent layers containing halide ions (Fig.1.3). Since the pressure affects primarily on weak bonding, as the pressure is increased, there will be large compression of weakly bonded X\(^-\) ions along the c-axis. Due to this anisotropic compression of electron charge density of X\(^-\) ions along the c-axis, the redistribution of electron charge density along a-b plane causes the distortion of the lattice [94]. The structural stability of these compounds is due to the combined effect of anisotropic coordination of the halogen X\(^-\) ions and the large polarizability of M\(^{2+}\) and X\(^-\) ions [94].

1.7.2 Raman Spectroscopy of Matlockites

In-situ Raman spectroscopy is a powerful tool to study the structural stability and lattice dynamics of matlockite compounds and is being used as a short-range order probe. The BaFX (X = Cl, Br and I) crystallizes in PbFCl type tetragonal symmetry D\(_{4h}\)\(^7\) or P4/nmm with two formula units per unit cell. The site symmetries of barium and halogen
(Cl, Br and I) atoms are $C_{4v}$ and at $D_{2d}$. Factor group analysis of the PbFCl compound with space group $P4/nmm$ and having two formula units in the unit cell, shows that the following vibrational modes can be expected at the centre of the Brillouin zone [95, 98-101]

$$\Gamma_{18} = 2A_{1g} + B_{1g} + 3E_g + 3E_u + 3A_{2u}$$

There are six Raman active modes namely $2A_{1g}$, $B_{1g}$ and $3E_g$, four IR active modes; $2A_{2u}$ and $2E_u$ and two acoustic modes; $A_{2u}$ and $E_u$. The modes $E_g(1,2,3)$ correspond to the atomic motion of M (Pb or Ba), Cl and F along b-axis. The modes $A_{1g}(1,2)$ belong to the anti symmetric vibration of M (Pb or Ba) and Cl atoms along c-axis. The mode $B_{1g}$ corresponds to the anti symmetric vibration of F-atoms along c-axis [99].

The pressure dependence of the phonon modes of BaFI compound is studied by Decremps et al up to the phase transition near 55 GPa [95]. They observed a large variation of Grüneisen parameter of the $A_{1g}$ phonon mode between 0 and 10 GPa and the variation is attributed to a gradual layer-nonlayer transformation of the compound under pressure.

### 1.8 Scope of the Thesis

This thesis focuses on two major themes. The first part discusses exploratory experiments to attempt synthesis of binary compounds like Ge-Sn, Ge-C and Pb-C formed from the elements involving group IV of the periodic table. These compounds cannot be synthesized by using conventional equilibrium techniques. But the synthesis can be possible by non-equilibrium techniques. For this thesis work, HP-HT route using Laser heated diamond anvil cell technique has been adopted. The second part of the thesis
reveals high pressure study of matlockite compounds in the form MFX where M= Pb and X=Cl or Br. This work is aimed at understanding the structural phase transitions in matlockite compounds.

This thesis consists of six chapters. Chapter II of this thesis presents the details of the various experimental tools and the characterization techniques used. Also it gives a brief description of pressure generating devices like Bridgman HP-HT cell and diamond anvil cell. The characterization tools used for this work viz high-pressure diffractometer that employs a RIGAKU rotating anode X-ray generator (UltraX 18) as the source and imaging plate detector, Raman spectroscopy and the angle dispersive X-ray diffraction facility at INDUS-2 are described briefly. Chapter III explains the synthesis of intra-group alloys/compounds involving group IV elements of the periodic table. The successful synthesis of Ge-Sn system by LHDAC technique as indicated by in situ Raman spectroscopy is discussed. Also attempts to synthesize Ge-C and Pb-C systems are presented in this chapter. Chapter IV describes high pressure structural behavior of matlockite compounds. The layered matlockite compounds such as PbFCl and PbFBr were synthesized using solid state reaction method and high pressure studies on these compounds was studied up to ~47 GPa and ~17 GPa respectively using X-ray diffraction technique. Similar to BaFX (X=Cl, Br or I) systems, PbFCl also undergoes pressure induced structural phase transitions in the sequence: tetragonal $\rightarrow$ orthorhombic at $\sim$18 GPa and orthorhombic $\rightarrow$ monoclinic at $\sim$38 GPa. In PbFBr, tetragonal to orthorhombic transition was observed at around 13 GPa. The bulk moduli of these compounds were obtained from their P-V variation and compared to similar matlockite compounds. Chapter V of this work presents high pressure Raman spectroscopy of PbFCl compound.
up to ~41 GPa. The pressure dependence of phonon modes of PbFCl at ambient pressure and also new modes formed at high pressures are also discussed. The variation of $A_{1g}(2)$, $E_g(2)$ and $E_g(3)$ modes with pressure are almost similar. But the behavior of $A_{1g}(1)$ mode with pressure is totally different. This mode shows an anomalous behavior. The anomalous behavior of this mode can be due to the weakly bonded adjacent chloride ion layers along the c-axis. The instability of $A_{1g}(1)$ mode above ~24 GPa is due to the change of nature of bonding from layer to non-layer type. The Grüneisen parameters of all the modes are calculated. Finally in chapter VI a summary of the thesis and potential future research relevant to the present work are discussed.

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