2. STUDIES IN HIGH PRESSURE PHYSICS

INTRODUCTION

The response of materials may depend upon the nature of high pressure loading viz. static or dynamic. In BARC, both kinds of studies are being carried out. The investigations under static high pressures are done using various kinds of diamond anvil cells (X-ray diffraction, Raman and resistivity), piston-cylinder device (compressibility) and WC Bridgeman anvils (transport properties). Single stage gas gun is used for the studies under shock loading. Using these, several materials – metals and alloys, organic and inorganic compounds and nano-crystalline materials have been investigated to obtain an equation of state and the nature of the phase transformations. This chapter provides a brief summary of the kind of investigations carried out over the last few years. This also includes the pulsed high energy density activity related to the high magnetic fields generated through capacitor bank or with the exploding foil accelerator.
2.1 EXPERIMENTAL CONDENSED MATTER PHYSICS: MATERIAL BEHAVIOUR UNDER HIGH PRESSURE

General nature of investigations being pursued are on materials of current interest/exotic properties, synthesized in-house or obtained through collaboration. A program for the investigation of Actinides and their compounds under pressure has also been initiated. Transport properties (R & TEP), Electronic transition, structural evolution, structural transition, P-V relation, HP-HT synthesis, comparison with theory (transition pressure, equation of state (EOS), details of electronic structure (anomalous EOS, Electronic Topological Transition, ETT, etc.) are the type of material behaviour being investigated. Variety of high pressure generating equipment like diamond anvil cells, piston-cylinder apparatus, and room temperature was confirmed by electrical resistance (R) data and details of the band structure.

In MgB$_2$, R measurements up to 30 GPa revealed a discontinuous fall by approximately 30% near 18 GPa. This is due to a phonon mediated ETT in MgB$_2$.

In Cd$_{1/2}$Hg$_{1/2}$, high-pressure angle dispersive X-ray diffraction measurements up to 40 GPa carried out at PURNIMA showed absence of any structural phase transition. However, the c/a ratio variation as a function of pressure show a small anomaly between 8 and 11 GPa. This anomaly could be due to the Van Hove singularity as observed in Cd and its isostructural alloys.


Diamond anvil cells-Diamond anvil cells have been adopted for angle dispersive X-ray powder diffraction, Optical spectroscopy, High temperature high pressure (HT-HP), and Electrical resistance measurements.

Toroid apparatus and Bridgman anvil apparatus have been fabricated and adopted to various measurements on condensed matter.

Electronic Topological Transition (ETT) at high pressures

An ETT involves changes in the Fermi surface topology, which takes place due to the modification of the band structure at extreme conditions of pressure. Transport properties and Equation Of State (EOS) are expected to show it’s signature. Several materials were investigated by electrical resistance and EOS measurements. In Zn the presence of an ETT near 10 GPa

Investigations on intermetallics with CaF$_2$ structure

Intermetallics with CaF$_2$ structure may undergo electronic and structural transitions and may transform into disordered phases under pressure. This is due to various reasons; most of them are entropy stabilized phases (volume expansion on compound formation), have partial covalent bonding, have a reduced transition metal d-orbital overlap etc. Several of these materials have been investigated (AuIn$_2$, AuAl$_2$, AuG$_2$, PtAl$_2$, NiSi$_2$) with several interesting results (Electronic transition, structural transition, disordered phases etc). An interesting example is that of NiSi$_2$. This material exhibits a change in sign of TEP at 0.5 GPa, and a gradual structural disorder under pressure.
Studies in High Pressure Physics

Electrical resistance, TEP and structure variation with pressure for NiSi$_2$
Investigations on strongly correlated systems

CuIr$_2$S$_4$ with spinel structure is a highly correlated system being investigated for several reasons. It exhibits interplay of structure, transition metal mixed valence (Ir$^{3+}$/Ir$^{4+}$), magnetic ordering, metal-insulator transition, Ir$^{4+}$/Ir$^{4+}$ dimerization, stabilization of an insulating phase at low temperature and high pressure etc. Investigations on CuIr$_2$S$_4$ revealed the existence of a re-entrant metallic phase in it above 30 GPa (Fig. a) and two structural transitions (Fig. b). The manganese based intermetallics, Mn$_3$GaC, with cubic antiperovskite type structure falls in to an intermediate class of materials between the rare earth manganites and the normal metallic alloys. High pressure angle dispersive X-ray diffraction investigations on Mn$_3$GaC up to 35 GPa (Fig. c) aimed at investigating the signatures of the strong interaction between the magnetic and the structural properties of Mn$_3$GaC on the compressibility and its structural stability under pressure did not reveal any anomalies.
Compressibility measurements on solids at high temperature in the piston-cylinder high pressure (PC) apparatus (Fig. a & b), were performed on fused quartz. An apparently first order transition in fused quartz with a volume change of about 20% at 3.6 GPa and 680 °C was observed (Fig. c). The X-ray powder diffraction (XRD) and Raman measurements (Fig. d) on the quenched sample showed the transition to be from a low density amorphous phase to another high density amorphous phase. This work is the first application of PC set up for high temperature compressibility measurement.

High pressure and high temperature studies on negative thermal expansion materials

Negative Thermal Expansion (NTE) is observed in the low-density phases of ionic compounds with MO₃, AO₃, AM₂O₇, A₂M₃O₁₄ and AMO₅ stoichiometry (A & M are octahedral and tetrahedral cations), which have a three-dimensional open network structures with corner sharing polyhedra. NTE materials predisposed to display interesting behavior at high pressure and high temperature. Also such ceramic materials that exhibit NTE are of technological importance because of the ionic conductivity facilitated by cation disorder in them and because of the possibility to tune the thermal expansion of NTE-normal material composites. On our ongoing investigations on these NTE materials we have carried out high pressure and high temperature investigations on Al₂(WO₄)₃, HfMo₂O₈, ZrMo₂O₈ and NbPO₄ belonging to a new subclass of compounds.

Several structural transitions, a linear pressure volume relation or unusually large variation of bulk modulus over limited pressure region, pressure induced amorphization that fall into two categories (Kinetic hindrance to bond reconstructive transitions and decomposition) and a possibility of synthesis of new phases at high temperature and pressure are the highlights of these investigations.

2.2 SHOCK WAVE PHYSICS RELATED ACTIVITIES

Gas gun facility at BARC

For studying the response of material to high stress and strain rates a gas gun facility has been developed at our laboratory (Fig.). The gun is capable of accelerating the projectile up to the velocity of 1 km/s, and generating the pressure of 40 GPa in the target material.

The gun has three main parts: breech, barrel and target catcher system. The breech contains a gas at high pressure and breech opening mechanism provides within a few milliseconds the unrestricted flow of gas behind the projectile. The barrel is a 3 meter long high tensile strength steel pipe with outer diameter of 114 mm and inner diameter of 63 mm. A straight slot, 3 mm wide and 1.9 mm deep, has been machined in the internal surface of the barrel. Also, a 2.5 mm long brass key with the same cross-sectional dimensions as that of slot is fitted to the projectile. This key is guided through the slot during the acceleration of the projectile and facilitates the impacts of inclined parallel plates for compression-shear experiments. The target catcher system consists of two sections separated by a thick mylar diaphragm. The first section (target chamber) permanently mounted to the muzzle end of the barrel is evacuated to 10 millitorr using a rotary and roots vacuum pumps. The second section is movable and contains the projectile and target stopping mechanism. The firing of the projectile is done with a remote control unit. The amplitude of the stress pulse in the target depends on the velocity of the impactor. The duration of shock (a few μs) in the target is determined by the impactor thickness (a few mm) and impedance of the impactor and target material. The projectile can be accelerated to the desired velocity by suitably selecting the breech pressure. Diagnostic techniques like electrical pins, manganin gauge technique, self shorting pins, ionization pins and optical pins are used for measurement of projectile velocity, shock pressure and shock velocity. A series of four pairs of electrical pins are used to measure the projectile velocity just before the impact. The manganin gauge technique is used for measurement of time resolved stress profile and shock velocity in the shock-loaded target. The self-shorting pins, ionization pins and optical pins are used to measure the shock velocity in the target. For investigation of shock induced structural phase transitions in powder or brittle sample a special capsule (recovery fixture) is used for holding the sample. In these experiments, termed as recovery experiments, shock pressure in the sample is determined indirectly from the hydrodynamic code in conjunction with measured projectile velocity. The sample recovered after unloading from peak shock pressure is characterized through X-ray diffraction and Raman measurements for any irreversible phase transition.

Theoretical Investigation of Pressure Induced Phase Transition in Ti at High Pressures

The group IV B elements are expected to undergo s-d electron transfer under pressure and, thus, mimic the transformation sequence \( \alpha \rightarrow \omega \rightarrow \beta \) shown by these elements with increasing number of d electrons on alloying with d-electron rich neighbors. This structural sequence under pressure is well established for Zr and Hf. However, Ti metal has been reported to undergo a transition from hexagonal phase (\( \omega \)) to an orthorhombic phase (distorted hcp, \( \gamma \)-phase) at 116 Gpa,
whereas there are also reports that titanium undergoes a transition to the $\gamma$-phase from the $\omega$-phase. To resolve this we have carried out total energy calculations employing the FP-LAPW method to examine the stability of the $\gamma$ and $\delta$ phase with respect to the $\omega$ and $\beta$ structures. Our analysis predicts at 0 K the $\omega$-phase transforms to $\beta$-phase via intermediate $\gamma$-phase, whereas at 300 K the $\omega$-phase transforms to $\beta$ structure directly and the $\gamma$-phase becomes most competing metastable structure in the pressure range of $\beta$-phase stability. The $\delta$-phase, however, is not at all stable at any compression. It suggests that the $\gamma$-phase observed in the experiments is a metastable phase that could be formed due to the shear stresses present in the experiments and the $\omega \rightarrow \gamma$ structural transition does not represent the phenomenon expected under hydrostatic conditions.

Calculated energy difference of the $\omega$ and $\gamma$-phase with respect to $\beta$-phase as a function of volume of unit cell. The curve ‘a’ corresponds to the $\omega$ phase; b, c , d, e and f correspond to the $\gamma$-phase with $y$ as 0.08, 0.10, 0.12, 0.14 and 0.16, respectively.

Free energy at 300 K plotted with respect to $\beta$-phase as a function of volume for the $\omega$, $\beta$ and $\gamma$ ($y = 0.1$) phases.


Ab-initio Calculations for Comparison of Hardness of Osmium and Diamond

On the basis of the high-pressure diamond anvil cell experiments on Os metal, Cynn et al. have reported that the bulk modulus of this metal is 462 GPa, higher than that of diamond (445 GPa), the hardest material known so far. Based on this they concluded that it has lower compressibility than diamond. We have reanalyzed the experimental data of Cynn et al and found that the bulk modulus of Os (434 GPa) and diamond are close to each other, implying that Os metal is as incompressible as the diamond but not more. We also, performed the first principles total energy calculations on Os and diamond using full potential linearised augmented plane wave method under both Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). For LDA calculation the value of $B_0$ estimated from Birch –Murnaghan fit is 461 GPa for
osmium and 464 GPa for diamond. From GGA calculations, this parameter is estimated as 436 GPa and 432 GPa, respectively, for the two elements. Thus, we find the theoretical values of $B_0$ for Os are comparable to the corresponding values of diamond for both LDA and GGA calculations.

## TEM Study on Shock Compressed Zr-20 Nb Alloy

The TEM study on shock compressed Zr-20 %Nb alloy have been done in collaboration with Materials Science Division, BARC. This alloy having bcc ($\beta$) structure at ambient condition was subjected to a peak shock pressure of 15 GPa in a 63 mm bore gas gun at our laboratory. The electron diffraction measurements of the retrieved sample confirmed the $\beta \rightarrow \omega$ transformation. The $\beta \rightarrow \omega$ transformation has been observed for the first time in an alloy under shock compression. The $\omega$-phase so formed has plate shape morphology and orientation relationship have been found same as that observed in $\omega$-phase formed on thermal treatment of the alloy. The formation of the $\omega$-phase has been explained on the basis of shear and shuffle of atoms on \{112\}$\beta$ planes.


## Theoretical Spall Strength and Equation of State of Materials in Negative Pressure Regime

The shock compression experiments generate not only the compressive high pressures but also high tensile stresses. Sophisticated diagnostic techniques like VISAR and ORIVIS, used recently to measure such tensile stresses, throw light on the material behavior in the negative pressure regimes. We have determined the ideal spall strength ($\sigma_s$) and also, the equation of state (EOS) in the negative pressure region for Mo and group IV B metals (Ti, Zr and Hf) from first principles total energy calculations using full-potential linearised augmented plane wave (FP-LAPW) method (WIEN97 Package). For Mo, we have calculated the ideal tensile strength ($\sigma_T$) and the elastic constants also. The $\sigma_s$ is calculated using uni-axial strain i.e. without allowing the Poison contraction, however for $\sigma_T$ the Poison contraction was also allowed.

The calculated $\sigma_s$ along \[1 0 0\] for Mo is 41 GPa as compared to the experimental value of 16.5 GPa measured after unloading the sample from peak pressure of 75 GPa (strain rate \~\!3\times10^7/s). Our calculated $\sigma_s$ value is 23 GPa. The calculated equilibrium volume is 15.96 (Å$^3$/atom, elastic constants $c_{11}$, $c_{12}$, $c_{44}$ are 439, 175, 100 GPa, and $B_0$, $Y(110)$, $Y(111)$ are 272, 339, 266 GPa, respectively.

For Ti, Zr and Hf we have determined $\sigma_s$ along [0001] direction for hcp ($\alpha$) and three atom hexagonal phase ($\omega$). The calculated $\sigma_s$ for $\alpha$ phase of Ti, Zr and Hf is 22, 18 and 20 GPa, and for the $\omega$ phase is 24.2, 19.5 and 23.6 GPa, respectively. The $\omega$ phase is found to be harder than $\alpha$ phase in agreement with available experimental results. The trend in the group IV B indicates that $\sigma_s$ for Ti is largest followed by Hf and then Zr for both $\alpha$ and $\omega$ structures. The theoretical $\sigma_s$ for Ti is much larger than for Zr and Hf.
higher than \( \sim 4.2 \) GPa measured at strain rates of \( \sim 10^6/s \). The bulk modulus of 110, 96 and 115 GPa, respectively for Ti, Zr and Hf, determined from the theoretical EOS in the negative pressure region, are in good agreement with experiments. The theoretical value of the \( \sigma_s \) for Mo and Ti are higher than the available experimental values. This discrepancy could be associated with the material defects, which dominantly control the spalling at such strain rates. For determination of ideal \( \sigma_s \), experiment should be performed at still higher stresses (and higher strain rates) to minimize the effects of material defects.

2.3 PULSED HIGH ENERGY DENSITY RELATED ACTIVITIES

- Pulsed High Magnetic Field Generation for Material Compression and EMP Generation Studies

High magnetic fields (greater than 100 Tesla) are generally produced in pulsed (\( \mu s - ms \) range) form using capacitor banks. These fields may be further enhanced through compression of metallic liners (cylindrical shells) in which initial magnetic field may be trapped and then compressed using secondary energy source such as another capacitor bank or chemical explosives. When the current is along the Azimuthal direction of the cylinder, the configuration is known as Theta-pinch or otherwise if it along the axial direction of the cylinder, the configuration is termed as Z-pinch. As a first step towards experiments on the mega gauss field generation at Applied Physics Division, field compression devices using Z-pinch and \( \theta \)-pinch as also single turn coils have been developed.

Experiments on Magnetic Field Generation for Material Compression:
Experiments have been carried out to investigate material compression using single turn coils made out of copper with 10 mm central hole for magnetic field generation. These coils have been fired on MAGIC-280 capacitor bank (340.8 mF/ 40 kV) at peak currents of 2-2.5 MA. An estimated peak magnetic field of 150-160 Tesla was produced in several shots. In some of the experiments, a titanium chip suitably confined in metallic layers to minimize the effect of induced currents (thereby avoid pre-heating) was placed to look for phase transitions.

Field compression device in Z-pinch configuration:
The Z-pinch field compression device consists of initial magnetic field system, accelerating field system and imploding liner system. The initial magnetic field system includes a coil and
2.5 mF/5 kV Capacitor bank. The bank is configured to give 60 kA at 100 micro-sec when charged to 5 kV. The initial field with suitably designed coil is about 8.52 kOe. The acceleration of the liner is carried out by 340 micro-F/40 kV MAGIC-280 Capacitor bank. The implosion velocity of the suitably designed liner is estimated to be about 0.317 cm/micro-sec when the bank discharge current is about 2 MA. Flux is compressed as long as the effective implosion speed exceeds the flux diffusion speed. When the two velocities become equal the compressed field will go through its maximum. With the sub bank charging voltage = 3.1 kV, MAGIC charging voltage = 25.2 kV, Triggered Spark gap voltage = 25 kV, probe calibration = 0.33 kOe/mv, the signal obtained from the center multi-turn probe is as shown below. From the measurements carried out using multi-turn magnetic probe at the center of the liner, the initial field has been estimated to be about 7.46 kOe, which is compressed to a maximum of about 40 kOe. Higher results are expected with better insulation design.

Field compression device in θ-pinchn configuration: In θ-pinchn configuration device, the MAGIC-280 capacitor bank is discharged through a thick single turn coil, with a thin liner placed co-axially. The liner (0.8 mm thick) is accelerated to maximum velocity of 0.7 cm/micro-sec, when the bank discharge current is about 1.07 MA. The maximum field obtained at the center is about 1.94 MOe, when the MAGIC charging voltage is about 16 kV and triggered spark gap voltage 25 kV. The signals obtained from the centrally placed 2-turn probe, are shown in figure.
Exploding Foil Accelerator (Electric Gun) with Opening Switch Action

Numerical analysis of electro-magnetically driven flux compression generator

Electro-magnetically driven flux compression generators are single shot and destructive in nature. To carry out prior analysis, we have developed a numerical model in “1-dimension”, considering the current distribution as a function of time. The circuit equation for axial current, azimuthal current, radius and inductance variation for each current, forms a set of ordinary differential equation. These first order differential-algebraic system of equations, \( g(t, y, y') = 0 \), are solved using the Petzold-Gear BDF method with given initial data for \( y \) and \( y' \). Neglecting the non-uniform deformation of the liner, which requires magneto hydrodynamic calculations, the center field obtained as per simulation is shown in the figure. The peak field at the center and the time to peak matches well with the published results.


Important Components of the EEF

Experimental assembly

Exploding foil accelerator (Electric Gun) is based on the explosion of a thin metallic foil when subjected to rapid ohmic heating due to passage of high currents in short duration. A thin plastic sheet placed in front of the exploding foil is then punched out as the exploded foil plasma expands into “barrel”. The velocity in such a system is highly sensitive to the rise time of the current. To experimentally demonstrate this fact and realize a higher velocity with the same capacitor bank system,
a concept of sharpening the current profile with an additional stage of exploding foil to act as a opening switch was adopted. A flyer velocity of 6.6 km/s, obtained with a single stage electric gun, was found to be enhanced to 7.4 km/s when additional stage was utilized. When properly optimized, it is expected to go up to twice the value using single stage. The flyer velocity was determined using a fast streak camera as well as a set of optical fibers.

As an extension of this work, an opening switch is being designed to generate MV/ sub-μs pulses while the electric gun is being developed along with necessary diagnostics to characterize energetic materials, which cannot be employed in large quantities.

**A Compact Pulsed Neutron Source Based on Plasma Focus Device**

Recently, a few compact Plasma Focus (PF) devices have been developed and operated at Applied Physics Division to generate pulsed neutrons on a routine basis. The device is like a narrow co-axial plasma gun. The narrow PF tubes are of 5 cm in diameter and 15 to 20 cm in length (Fig.). The central anode and the outer cathode are made of stainless steel. Smooth and non-porous alumina ceramic sleeve is used as insulator at one end of the tube. Commercially available high purity alumina ceramic tubes are polished to make these tubes compatible to the PF operations. A capacitor bank (Fig.) made with a capacitor of 7.2 μF is used as the energy source.

Signals from dI/dt loop and a set of 3 photodiodes (a) Single exploding foil and (b) two exploding foils.

Typical Signals from PF X-rays (top two) and neutrons current derivative (bottom).
Conventional power supply and trigger units based on electricity supply were employed to charge and discharge the capacitor bank through the plasma focus device. But to make it portable type, for one of the plasma focus devices, the capacitor bank was charged to same voltage by a battery based power supply. The trigger unit of the spark gap used to discharge the capacitor through the PF device was also battery based.

A calibrated silver activation detector and two plastic scintillator detectors are deployed for the measurements of emitted neutrons. The current derivative is monitored by a Rogowski loop. The device is normally operated at 25 kV at a deuterium filling pressure of 6 mb. Pulsed 2.45 MeV neutrons of $\approx 10^7$ neutrons/pulse are generated due to D-D reaction. The pulse width of the neutron is 25 – 30 nS.

With some modification and dimensional optimization of the plasma focus device it is expected to generate $\approx 10^8$ neutrons/pulse for which work is in progress.

### 2.4 MECHANICAL RESILIENCE OF SINGLE-WALLED CARBON NANOTUBES (SWNTS)

Single walled carbon nanotubes (SWNTs) are known to form two-dimensional triangular lattice by self-organizing into bundles. Our high pressure X-ray diffraction experiments, carried out with synchrotron X-rays, along with Raman measurements provide the understanding of the mechanical properties. X-ray diffraction studies on (11,11) SWNTs show that, under hydrostatic pressures, the radial strain is released prior to the reversible loss of lattice order in SWNTs.

Under non-hydrostatic pressures, the lattice order is found to vanish at $\approx 2$ GPa, which becomes irreversible for compression beyond 6 GPa, in sharp contrast to our studies under hydrostatic conditions. Moreover, nanotubes are found to be much more compressible under non-hydrostatic conditions (bulk modulus (B) $\approx 10$ GPa) than under hydrostatic pressures (B $\approx 34$ GPa). However, the reappearance of the radial breathing modes (RBM) and tangential modes (TM) on release of pressure in the Raman measurements implies that the ordering of tubes in the pressure quenched SWNT bundles is marginally regained, with short coherence length, but not enough for the re-emergence of X-ray diffraction peaks.

_characteristic diffraction ring of the SWNTs at various hydrostatic pressures, (a-c) for increasing pressure and (d) for decreasing pressures [Pattern recorded at BL10XU beamline of SPring8 synchrotron].

Variation of d-spacings under various non-hydrostatic (filled circles) and hydrostatic (open circles) pressures.

2.5 STRUCTURAL AND MAGNETIC BEHAVIOUR ON Fe-FILLED MULTI-WALLED CARBON NANOTUBES (MWNTS)

High pressure angle dispersive X-ray diffraction experiments, were carried out up to ~20 GPa, at the 5.2 R beamline of the Elettra synchrotron. Encapsulated iron inside nanotubes is found to be in the form of α-Fe and Fe₃C. Unlike pristine MWNTs, the intertubular distances \(d_o\) for the filled tubes undergo a sharp change at ~9 GPa, as shown in Fig., possibly due to polygonization of the tubes. Mechanical properties of α-Fe and Fe₃C are found to be very different (more compressible) from their bulk counterparts. The structural transition in MWNTs is coincident with an iso-structural phase transition in Fe₃C at ~9 GPa, in sharp contrast to the absence of a transition in the bulk Fe₃C up to 70 GPa.

Magnetic behaviour of Fe-filled MWNTs has also been investigated with the dc magnetization measurements. Our results show that the encapsulated nanowires form one dimensional exchange coupled ferromagnetic system. Observed saturation magnetization, \(M_s\) (~85 emu/g), of the composite nanowires is found to be significantly less than the expected value. The observed low temperature hysteresis loop shift in the field cooled (FC) case, earlier explained in terms of the onset of antiferromagnetism in fcc Fe (γ-phase) at low temperature (<50 K) and its exchange coupling with the α-Fe (assuming that α-Fe and γ-Fe in the nanowire have a common interface). However, as our data shows the negligible abundance of γ-Fe, we feel that the hysteresis loop shift originates from the occurrence of exchange bias due to the disordered surface spins of the Fe nanowire.


2.6 IRREVERSIBLE AMORPHIZATION OF NEGATIVE THERMAL EXPANSION MATERIALS

Negative thermal expansion behavior (NTE) of the substances is useful in helping design materials with the appropriately tuned coefficient of thermal expansion. Some of the important NTE materials are zircon, zirconium tungstate, \(A_2(MO_4)_3\) compounds (where \(A=\)Al, Sc, Lu, Yb, Tm, Er, and Y and \(M=\)Mo, W etc.). We have studied the high pressure behavior of some of these compounds like \(Y_2(WO_4)_3\), \(Al_2(WO_4)_3\), \(Sc_2(WO_4)_3\) and a double molybdate \(KSc(MoO_4)_2\) using X-ray diffraction and Raman scattering techniques. \(Y_2(WO_4)_3\) is known to have the largest isotropic negative thermal expansion in this set of materials and our experiments show that it also has the largest NTE stability range. We have observed that \(Al_2(WO_4)_3\) and \(Sc_2(WO_4)_3\) show several phase transitions to lower symmetry structures prior to the transformation to a highly disordered state at ~7 GPa, whereas \(Y_2(WO_4)_3\) amorphize directly at ~4 GPa. In all these materials it was observed that the high pressure disordered phase is retained on release of pressure. Earlier studies had suggested that pressure induced amorphization in these materials maybe related to the softening of the transverse acoustic modes responsible for NTE. Even though, amorphization of yttrium tungstate supports this suggestion, the presence of precursor monoclinic phases prior to amorphization in \(Sc_2(WO_4)_3\) and \(Al_2(WO_4)_3\) raises a doubt on this relationship, as the monoclinic phases are known not to exhibit negative thermal expansion.
Several geologically important minerals of the earth’s crust exist in the tetrahedral framework structures, made of corner linked tetrahedral units. The corner linkage acts as a flexible hinge between the tetrahedra, permitting the existence of several polymorphs. Therefore, it is expected that silica polymorphs like quartz, cristobalite etc. and the iso-structural materials like berlinite, orthorhombic AlPO$_4$ etc. would show phase transitions. In particular, the pressure induced structural modifications of these materials provide important information for the modeling of the transition zone between upper and lower mantle of the earth. We have studied several of these compounds using experimental and theoretical techniques like X-ray diffraction, Raman spectroscopic studies, classical and first principle molecular dynamics.


Our recent Raman spectroscopic and X-ray diffraction studies have shown that cristobalite form of AlPO$_4$ transforms to Cmcm phase at 8.1 GPa under hydrostatic pressures. The new Cmcm phase is found to be stable even at ~ 40 GPa and 310ºC. To understand the mechanism of this transformation, we have carried out classical molecular dynamical as well as the first principles structural relaxation calculations. Fig. shown delineates the path of this transformation.
2.8 SCHEELITE STRUCTURED COMPOUNDS

Scheelite structured alkaline earth tungstates and molybdates are used as scintillators, cryogenic detectors of dark matter and are potential candidates for the laser host materials. Recently molybdates and tungstates have been the focus of high pressure studies to understand the structural stability in these compounds. Some of the earlier studies on the scheelite compounds had suggested that due to the packing efficiency wolframite would be a preferred high pressure phase for these materials. However, some of the recent high pressure studies have shown that these compounds may not transform to this phase.
We have carried out high pressure Raman and X-ray diffraction studies on BaWO$_4$, BaMoO$_4$ and PbWO$_4$. It is observed that all the three compounds undergo phase transitions to the lower symmetry phases at high pressures. The first transformation was at 7 GPa, 6 GPa and 7.5 GPa respectively. In barium tungstate and barium molybdate this high pressure phase is similar to a distorted scheelite structure (Fergusonite). Figure shows the two structures as determined by us. The second high pressure transition is at 14 GPa, 14 GPa and 10 GPa respectively. On release of pressure the high pressure phases transform back to the initial scheelite phase. From these studies it appears that the high pressure behavior of the molybdate and tungstate is similar. The temperature induced scheelite to fergusonite phase transition is known to be ferroelastic, associated with the phonon mode softening in the scheelite phase. The observed reversibility suggests similar mechanism for the high pressure behaviour.


2.9 MOLECULAR SOLIDS UNDER HIGH PRESSURES

- Pentaerythritol

Interatomic interactions in the molecular solids range from weak van der Waals to strong covalent or ionic type. Therefore, the high pressure studies of molecular solids are interesting, as the compression brings about a reduction in the intermolecular distances, causing significant variations in the interaction energies, which, could also lead to phase transformations. Several molecular solids like pentaerythritol, Amino acids, DL serine and alpha glycine have been studied with the help of Raman and X-ray diffraction studies. Some of these have shown changes in the strength of the hydrogen bond with pressure whereas pentaerythritol and DL serine have shown structural changes.

Specially Pentaerythritol (C(CH$_2$OH)$_4$) which has a structure closely related to that of pentaerythritol nitrate (PEN) (used as an initiating explosive, the explosive sensitivity of which seems to be related to its structural features) has been studied with the help of Raman and synchrotron based IR and X-ray diffraction measurements. Our results show that this compound undergoes transformations to a lower symmetry phase between 5.2-5.9 GPa. It further undergoes phase transformations at ~ 8.5 and ~ 11 GPa; eventually evolving to a disordered phase beyond 14-15 GPa. All the structural changes are found to be reversible. The initial tetragonal phase was retrieved on Diffraction pattern of (C(CH$_2$OH)$_4$) at different pressure release of pressure from 18.5 GPa.


- TCNE

High-pressure Raman scattering studies of the cubic and monoclinic polymorphs of tetracyanoethylene (TCNE) have been carried out. The evolution of the Raman spectrum with pressure suggests that the cubic form is stable up to about 8 GPa and the sample becomes opaque to visible light above 14 GPa. In the monoclinic phase, changes in the Raman spectrum indicate a subtle phase transition above 3.6 GPa and at higher pressure the sample progressively becomes black, similar to what has been observed in the cubic phase.
The Raman spectrum of the sample above 7 GPa is indicative of polymerization of TCNE. The spectrum of the pressure cycled opaque phase shows broad features characteristic of an amorphous phase, which is understood as being due to random cross-linking of TCNE in the pressure reducing cycle.


2.10 DEVELOPMENT OF HIGH PRESSURE OPTICAL ABSORPTION SET UP: STUDY ON RED-HgI₂

For the absorption studies under high pressures, a diamond anvil cell based high pressure optical absorption set up has been developed in the transmission geometry. This system can scan over 1.4 – 3.5 eV range. Using this, the band gaps can be determined with an accuracy of 0.005 eV. The sampling area for these measurement is ~10 micron (yellow spot on the sample, in Fig. (a). The output signal is detected by lock-in technique which has been configured with the PC by the CVI software. Any visible change of the sample can also be recorded with the online viewing arrangement with the system.

(a) 0.1 MPa  
(b) 1.26 GPa  
(c) 1.4 GPa  
(d) 4.9 GPa  
(e) 11.8 GPa  
(f) 0.1 MPa (released)

Microphotographs of red-mercuric iodide single crystal in the gasketed diamond anvil cell taken at different pressures. The yellow dot in (a) shows the focused spot.
Using this technique, we have measured the pressure induced variations in the band gap of mercuric iodide. Our results show that it undergoes direct – direct – indirect gap transitions at 1.3 and 7 GPa respectively. The observed pressure dependence of the band gap suggests that, in the absence of any more phase transformations, HgI$_2$ may metallize at ~40±6 GPa. Combining with the compressibility results obtained from the X-ray diffraction measurements, it is found that in the tetragonal phase, intra-layer covalent bond deformation potential is much stronger than the van der Waals bond deformation potential and these are of opposite sign.