Abstract: It has been shown that high-pressure polymorphs of simple materials often display novel thermal/mechanical/optical properties and can be recovered at ambient conditions with significant stability (or metastability). Therefore, high-pressure synthesis of such materials offers an avenue toward novel materials applications. However, the present high-pressure method of diamond-anvil cell (DAC) or large volume press (LVP) has a fairly limited use in this regard because of a small amount of sample or the lack of in-situ optical diagnostic, respectively. Hybridizing the merits of DAC and LVP, we have recently developed a simple yet unique device, called a Transparent Large Anvil Press (TLAP), which consists of an opposed diamond anvil cell and a Paris-Edinburgh press. Coupling with a wide range of optical diagnostics such as Raman spectroscopy and laser heating, the TLAP is capable of in-situ investigation and synthesis of a milligram quantity of cryogenic samples at high pressures and temperatures.

1. Introduction

Application of high pressure on materials has resulted in considerable change in its physical and chemical properties. Recent experiments have also demonstrated that high pressure and temperature is a very powerful tool to synthesize new stable and metastable phases of low Z elements [1-3]. For many materials, such high-pressure modifications can be conserved in metastable form at ambient conditions for a significant amount of time [4]. Discovery of novel properties like optical nonlinearity [5], high energy density [6] and super-hardness [7] of the high pressure polymers of several low Z compounds, specifically, CO$_2$, N$_2$, CO to name a few, have opened up new prospects of their applications in science and technology [8,9].

Almost all of the high pressure-high temperature synthesis experiments reported in the literature has been performed by using microscopic quantities of samples in diamond anvil cells (DACs) at formidable high pressure-high temperature conditions [10,11]. This restricts the characterization of the novel properties of the materials by using conventional techniques like differential scanning calorimetry, solid state NMR or other mechanical testing tools, which typically require large milligram quantities of samples.
Large-volume presses (LVPs) such as a multi-anvil press or the more compact Paris-Edinburgh cell (PEC) even though more suitable for compressing milligram to gram quantities of sample to few tens of GPa, are mainly used for X-Ray and neutron diffraction measurements [12-14]. The main reason being they typically use opaque WC or sintered diamond anvil assemblies which severely restricts in-situ optical or spectroscopic diagnostics. Additionally, the extraordinarily large mass of the press components prevent efficient cryogenic loading of many gaseous samples at ambient conditions. This has also limited the types of samples that can be studied using LVPs to those which are either solids or liquids at ambient conditions.

There have been recent efforts which have tried to address the above issues in LVPs systematically; however in most of the cases, optical information from the sample chamber were limited to ruby fluorescence measurements. The techniques used either a sequence of NaCl window plugs [15] or optical fibers fixed into a ceramic tube with molten glass [16]. There have been other approaches too; using multi-anvil apparatus [17] or large sapphire ball cells using anvils ranging from 0.5 to 1 inch in diameter [18] and even large synthetic sapphire anvils [19]. However, these devices cannot be considered to be LVPs in the strict sense of the term, they were more of the pressure cell type.

On the other hand, there have been very few efforts to address the issue of cryogenic loading of samples inside LVPs; the most notable ones being that of Klotz et al. [20] where he successfully loaded deuterated CH\textsubscript{4} and NH\textsubscript{3} in a PEC at liquid nitrogen temperatures even though the technique had its safety concerns due to the amount of energy stored in the hydraulic fluid system. The other method was pioneered by Lipp et al. [21] where they thermally isolated the sample/gasket/anvil area and incorporated a leak-tight sample containment chamber which they used to load CO. However, this whole procedure required a long time because of the multiple steps involved and also used several resistive heaters to warm the LVP up to ambient temperature before the actual experiments could be started. Another point to note in both the above works is none of the LVP assemblies allowed optical access to the sample chamber.

In this work, we present a relatively simple, portable and unique approach to using the modified version of the PEC using a separate cell assembly with either WC or sintered diamond (SD) seats and opposing diamond anvils in the Bridgman configuration. A key feature of this type of design is it allows efficient and prompt loading of samples under cryogenic conditions as well as provides optical access to the sample chamber for in-situ laser heating, Raman and other spectroscopy measurements. We demonstrate the application of this modified PEC, or Transparent Large Anvil Press (TLAP) by loading liquid N\textsubscript{2} and liquid CO\textsubscript{2} samples and by performing Raman spectroscopy measurements on them. Additionally, results of in-situ laser heating on CO\textsubscript{2} samples at pressures greater than 15 GPa using this assembly and efforts to recover novel phases of tetracyanoethylene (TCNE) are also presented. Both the experimental arrangement for optical measurements and the mechanical design of the complete PEC assembly are very general and can be adapted to a wide variety of different LVP configurations currently in use among numerous high pressure and geo-physical research communities.

2. Design of the TLAP & optical arrangement
In our mechanical design of the cell assembly, we use the systematics of the PEC, which operates by injecting hydraulic fluid into the reservoir of a piston/cylinder cavity which, in turn, applies the force on the sample that is studied. The applied load is determined by the hydraulic fluid pressure and the cross-sectional area of the piston surface of the reservoir.

Following is the modification that we incorporated in a 200 ton VX2 type PE press for our experimental measurements. We introduce a separate cell assembly between the steel spacer of both the breech and the piston sides of the PEC (see Figs. 1, 2a) that allows the sample chamber to be portable and eases the procedure of cryogenic loading. This separate assembly which is made of Vascomax maraging steel and subsequently heat-treated after final testing is carried out, houses the
WC (supported by Vascomax maraging steel) or GE Compax SD (supported by WC) seats with opposing diamond anvils in the Bridgman configuration (see Figs. 2 b,c).

Figure 1. Internal schematics of the TLAP. The portable arrangement on the right has been designed in-house at WSU for portability and optical access inside the TLAP. The center portion of the PEC (white area between the WC supports [13] in the left figure) is where the portable arrangement on the right is placed after loading the sample. After this, the hydraulic arrangement of the PEC is used to increase the pressure. For further details, please see text.

The outer dimensions of this portable cell assembly is custom made to fit inside our cryogenic gas loading device, that has been demonstrated to be very effective in loading gaseous samples in DACs by condensing them to a liquid under appropriate P-T conditions [22]. The WC (SD) seats have funnel shaped access holes drilled in the center which merge into a 1 mm straight bore before opening up into an inverted cone that had been precisely cut to accept the diamond (moissanite) anvils (see Fig. 2d). The diamond (moissanite) anvils having a height of 2 mm are 45° crown angled and are obtained from Almax Industries (Charles and Colvard).

Finally, after the alignment of the diamonds is complete so that they are centered with the entire seat arrangement, STYCAST 2850T is used as an epoxy to hold them in place even under cryogenic conditions. Initially to close the cell after the sample has been loaded, the screws are used to apply the pressure. To avoid any ambiguities, there is a notch that is machined in into the top and bottom parts of this portable cell assembly so that it can be perfectly aligned with the backing plates both on the piston and the breech side of the PEC that would allow us to evenly distribute the hydraulic load across the sample area during actual measurements.
We employ a standard confocal micro-Raman system in back-scattering geometry to collect the Raman signal with some differences as mentioned below. For ease of incorporation of the TLAP system in our current optical table, we use 200 µm core multi-mode optical fibers to collect and deliver the Raman signal to the Princeton Instruments Acton 2500 spectrometer (see Fig. 3).

![Experimental arrangement used for in-situ laser heating and Raman spectroscopy inside the TLAP. The inset shows the internal schematics of the small cell that is used in the measurements.](image)

**Figure 3.** Experimental arrangement used for in-situ laser heating and Raman spectroscopy inside the TLAP. The inset shows the internal schematics of the small cell that is used in the measurements.

Stainless steel gaskets having initial thicknesses ~ 300 µm were used to contain the samples (N₂ or CO₂ with multiple ruby chips) in a hole of diameter 2.5 mm. Long WD Mitutoyo objectives were used to deliver (collect) the optical signal to (from) the sample chamber which was combined with a lens system to image the sample chamber onto a camera (magnification: 3×, WD = 75 mm).

3. Experimental Results

Fig. 4 shows a typical plot of correlation of the applied load with the pressure inside the sample chamber (for TCNE samples) as obtained from the ruby fluorescence technique. It is seen that we are operating the PEC in the linear regime and so the stresses are distributed evenly.

![Plot of load and oil pressure vs Ruby fluorescence measurements. The calculated ratio F/A (assuming the area of compression to be that of the diamond/moissanite table) shows the pressure multiplication factor, m ~ 2.5; which is in stark contrast to the assumption of a parabolic pressure profile.](image)

**Figure 4.** Plot of load and oil pressure vs Ruby fluorescence measurements. The calculated ratio F/A (assuming the area of compression to be that of the diamond/moissanite table) shows the pressure multiplication factor, m ~ 2.5; which is in stark contrast to the assumption of a parabolic pressure profile.

### 3.1 Nitrogen (N₂ measurements)

A 300 µm thick spring steel gasket was pre-indent ed using the PEC to about 280 µm and a hole of diameter 1.5 mm was drilled using a standard drilling machine. A few micrometer sized ruby chips were scattered inside the cell for in-situ pressure measurements. Liquid N₂ was then cryogenically loaded onto the maraging steel-WC-diamond anvil cell assembly by immersing the cell into a bath of liquid N₂. All the four screws were used to close the cell inside the liquid and the loading pressure after the cell had warmed up to room temperature was ~ 3 kbars. The cell assembly was then inserted into the PEC and the pressure was increased using the hydraulic mechanism. The oil pressure and
subsequently the load on the sample chamber could be controlled with a high degree of accuracy, which allowed in-situ ruby fluorescence measurements to estimate the pressure inside the sample chamber.

Fig. 5 shows a succession of the in-situ Raman spectra of Nitrogen starting from 3 GPa to about 14 GPa. It shows the fact that nitrogen freezes around 5 GPa in the δ phase which shows the two stretch modes ($\nu_1$, $\nu_2$) unique to this phase [23]. Their frequency increases steadily as the pressure is increased as does the relative spacing between the two Raman peaks. The sample size as is shown in the sample microphotograph (see Fig. 4) is about 1.5 mm in diameter and we estimate that the thickness of the sample at the highest pressures to be of the order of 100 µm. Because of the large area of the sample chamber, we are also able to make highly accurate spatially resolved ruby fluorescence data to know the actual pressure inside the sample chamber.

Figure 5. Sample microphotographs for N$_2$ inside the modified PEC assembly at a pressure of around 6 GPa. The scattered particles are ruby crystals. The right panel shows the successive Raman spectra of N$_2$ starting from a liquid at the loading conditions to about 14 GPa.

Further increase of pressure beyond 14 GPa resulted in fracturing of the anvils accompanied by a significant loss of pressure. The post-experimental observation showed that the WC seats have fractured radially which is not unexpected since WC anvils are known to fail around 10 GPa.

3.2 Carbon Dioxide (CO$_2$) measurements

To overcome the limitations of using WC seats, the measurements on CO$_2$ were taken using the WC-SD-diamond anvil cell assembly. After preparing a gasket on the same lines as above, CO$_2$ samples were loaded in the small cell assembly from a liquid by condensing CO$_2$ gas to -35 °C and 15 atmospheres. Besides ruby chips, a thin Pt foil (10 µm) was placed in the sample chamber to heat the CO$_2$ sample using laser powers around 10-30 W. The time taken to complete the entire process from starting the condensation of the gas to a liquid followed by subsequent loading of the liquid sample inside the cell and then warming up the cell to room temperature takes about 30-35 minutes.

The cell assembly was then inserted into the PEC and the pressure was increased using the hydraulic mechanism as in the earlier measurements. Figs. 6b and 6a show the microphotograph of the sample chamber and results of Raman measurements on this sample starting from as low as 3 kbars which show the onset of transformation of CO$_2$ from a liquid to the ‘dry ice’ form (CO$_2$-I) starting around 13 kbars and finally transforming to a mix of CO$_2$-I and III above 130 kbars [24, 25].

The pressure was measured using the ruby fluorescence technique and it was found that there is no appreciable pressure gradient across the sample at these pressures.

We also did in-situ laser heating of CO$_2$ inside the modified PEC at pressures around 16 GPa when the mix of CO$_2$-I and III transforms to CO$_2$-IV and II [26] along the direction of decreasing temperature gradient. Fig 6c shows the Raman spectrum of this transformation. Due to the large sample chamber in the TLAP, measuring the Raman spectrum along the temperature gradient was trivial as compared with our earlier laser heating measurements inside DACs [22].
Figure 6. Experimental results using CO$_2$ as the sample in the modified PEC assembly. (a) Successive Raman spectra of CO$_2$ using our modified PEC assembly. (b) CO$_2$ sample microphotograph at 3 kbars, (c) Raman spectra of laser heated CO$_2$ around 17 GPa inside the TLAP.

3.3 Tetracyanoethylene (TCNE) measurements and sample recovery

Owing to its high electron affinity, TCNE molecule forms many charge transfer complexes with a variety of electron donors. These charge transfer complexes exotic electrical, magnetic and other chemical properties [27, 28]. Interesting TCNE-based compounds have also been synthesized [29] wherein the magnetization states can be switched using visible light of different wavelengths. TCNE is also known to polymerize under different physical conditions, which can find applications in several electronic devices [30]. Figure 7 summarizes our results on Raman measurements using WC anvil assembly and our efforts on recovering the novel polymeric phase. The measurements show that TCNE undergoes amorphous transformations on pressure release to give very broad graphitic-like D-G band Raman spectra.

Figure 7. TCNE sample recovery. (Left) Raman spectra of TCNE from ambient conditions to about 8 GPa, when it starts polymerizing. The ruby was at the edge of the sample and so the sample pressures would be at least 15-20% higher than labeled. (Right Top) Raman spectra of recovered TCNE sample after pressure cycling, indicating a possible amorphization. (Right Bottom) Sample microphotograph of the recovered TCNE sample outside the TLAP. The sample is transparent to begin with, however, it becomes black on polymerization and remains black on subsequent sample recovery.
4. Conclusions
We have successfully demonstrated an optically transparent anvil design assembly that could be used for in-situ laser heating, optical spectroscopy measurements and also efficiently load condensed gas samples inside the sample chamber for use inside LVPS like the PEC. Our TLAP design permits high quality imaging of the samples both at ambient conditions and under pressure inside the modified PEC, which is necessary while doing laser heating or photo-catalysis measurements. Pressures in excess of 15 GPa have been achieved using our current design of WC-SD-diamond anvil assembly with macroscopic quantities of samples several mm in diameter, which will allow the convenient use of routine characterization tools like DSC and NMR spectroscopy on the recovered samples.

5. References
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