Development of laser-heated diamond anvil cell facility for synthesis of novel materials

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Investigation of material behaviour under extremely high pressures and temperatures using IR laser-heated diamond anvil cells (DACs) has emerged in the recent years as an important area of research, both basic and applied. This article presents details of a laser-heated DAC facility that we have recently set up at our laboratory. The facility consists of a suitable arrangement of a CO_2 laser, motorized translation stages, a Mao–Bell-type DAC, IR and visible optical assembly, CCD-based monochromator, etc. Also, the facility has the capability of pressure measurement using Ruby fluorescence method and temperature measurement using spectroradiometric technique. With this facility, materials can be subjected simultaneously to high pressures and temperatures ($P_{max} \sim 100$ GPa; $T_{max} \geq 5000$ K). Results on successful synthesis of InSb by direct elemental reaction and on a preliminary experiment wherein direct conversion of graphite to a transparent phase has been attempted with this facility are also presented.

Keywords: Diamond anvil cell, high-pressure, laser-heating, novel materials.

THE diamond anvil cell (DAC) is a unique device to generate high static pressures on matter[1]. With the DAC it is possible nowadays to investigate materials at pressures up to a few megabars[2,3]. High strength of the diamonds coupled with their excellent transmittance to almost the entire electromagnetic spectrum has led to extensive *in situ* studies on a myriad of pressure-induced phenomena in materials using techniques such as the X-ray diffraction, Raman and Brillouin spectroscopy, luminescence spectroscopy, Mössbauer spectroscopy, etc. up to several megabars[2]. The work done in compressing the system of interest to such high pressures is typically of a few electron volts, and is comparable to the chemical bond energies[4]. This can induce large changes in the behaviour of electronic orbitals and as a result increase the reactivity of the species under study. In addition, heating of the sample squeezed inside the DAC can provide the kinetics necessary to induce novel reactions between the reactant species by overcoming activation barriers that are otherwise impossible to do so at ambient conditions[4,5]. This paves the way for synthesis of novel materials which may have exotic mechanical,

optical or electronic properties. Samples inside a DAC can be heated either by internal or external methods. The internal heating method involves resistive heating of the sample by passing an electric current through a miniature heating assembly or by directly passing the current through the sample, if it is conducting[6,7]. This poses difficulties like sample contamination and frequent breaking of the electrical leads which are taken into the DAC sample chamber that can limit the pressure capability. Temperatures of ~2000–3500 K have been achieved by this method[7]. In the external heating method, either the DAC as a whole is heated by placing it in a furnace or the cavity just around the diamond anvils is heated with a heater coil. Either way, limitations arise in terms of weakening of the structural materials constituting the DAC in this external heating method, thereby limiting experiments[7] to temperatures ~1700 K.

Another way of externally heating the sample is by means of focusing an infrared (IR) laser beam directly onto the sample. The wide-range transmittance of diamonds to almost the entire electromagnetic spectrum allows focusing of high-power IR lasers onto the sample squeezed in the DAC, thereby subjecting it simultaneously to high temperatures[8] of over 7000 K and pressures of over many megabars. Typically these kinds of pressures and temperatures exist in planetary interiors. This technique, called the laser-heated diamond anvil cell (LHDAC) technique, first attempted successfully by Bassett and Ming[9,10] in the early 1970s, has been emerging in recent years as a preferred route for investigating materials and synthesizing novel phases in the hitherto unexplored *P–T* region. Some of the advantages in using this technique are: (i) extremely localized direct heating of the sample alone; (ii) contamination-free sample chamber while using inert gas as pressure medium; (iii) amenability of the DAC for a variety of *in situ* characterization methods like X-ray diffraction, spectroscopy (Raman, IR, UV, visible); (iii) large pressure and temperature ranges that simulate intra-planetary conditions, (iv) high quenching rates, etc. Small sample quantities (μg), and *P–T*-dependent absorption of heating IR laser wavelengths by the samples, pose some of the limitations of this technique.

Chandra Shekar *et al.*[11] discuss the recent exciting developments in the LHDAC field. Synthesis of nitrides of C, B, Si and Ge that are expected to rival diamond in terms of hardness, is currently one of the frontline prob-
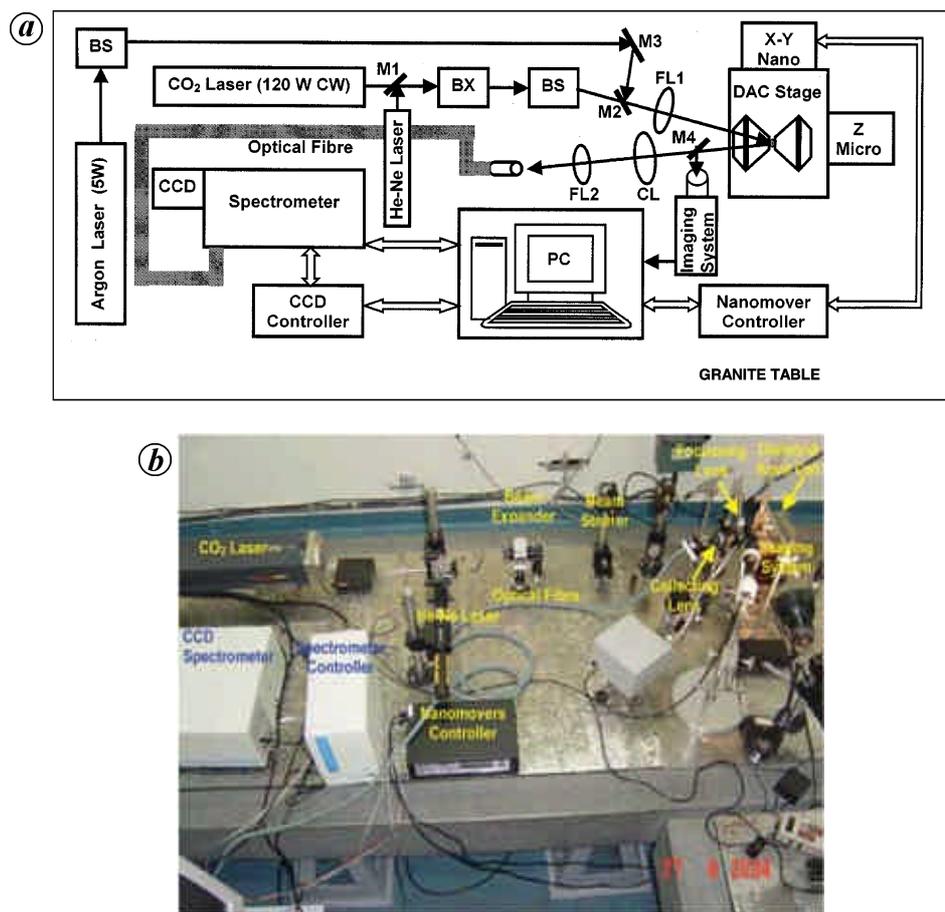
Figure 1. *a*, Schematic of the LHDAC set-up. M1–M4, Mirrors; BS, Beam steerer; BX, Beam expander; FL1 and FL2, Focusing lenses; CL, Collecting lens. *b*, Photograph of the set-up. All components, including lasers are mounted on a granite table located on a special foundation, structurally isolated from the rest of the building to minimize vibrations.

lems addressed by LHDAC researchers[11]. Other applications of LHDAC include investigation of melting phenomenon and structural transitions in a variety of materials, investigation of *P–T* behaviour of geophysically important minerals like silicates, sulphates, oxides, etc.[12] and establishment of the phase diagram of iron[13,14].

At our laboratory in Kalpakkam, we have recently set up a state-of-the-art LHDAC facility to address some of the above applications in general and explore the synthesis of novel phases of materials in particular. The challenge that beset us was (a) in setting up the optics and accomplishing heating of a ultra tiny sample (~75 μm diameter) that is sandwiched at high pressure between the two diamond anvils of the DAC to very high temperatures using the invisible IR laser beam, without causing any damage to the diamonds and other supporting materials; and (b) to enable simultaneous viewing of the sample being heated, measurement of its thermal emission spectrum for temperature estimation and record fluorescence spectrum of a ruby placed near the sample for pressure estimation.

Description of IGCAR LHDAC facility

Figures 1 shows a schematic diagram and photograph of the LHDAC facility set up at IGCAR, Kalpakkam. An indigenously developed Mao–Bell-type DAC capable of generating pressures up to 100 GPa (1 Mbar)[2], a 125 W CW CO_2 laser (l = 10.6 μm; TEM_{00} mode), a 5W Argon ion laser, a CCD-based spectrometer, a *X–Y* nanomotion system and an imaging system are the essential constituents of this set-up. Some of the salient aspects of this set-up are given here.

IR optics

A He–Ne laser beam (l = 632.8 nm) is first made to traverse the same path as the CO_2 laser beam. Alignment of the CO_2 laser-compatible optical components like the beam expander (BX), beam steerer (BS) and focusing lens (FL1) is then done with the visible He–Ne laser. Final focusing of the CO_2 beam (spot size ~40 μm) is achieved at

the centre of the sample inside the DAC by manipulating the beam as well as the DAC XYZ stage with a PC-controlled nanomotion system.

Nanomotion system

In heating experiments with the LHDAC facility, a critical requirement is that the focused IR laser beam should fall exactly on the sample squeezed inside the DAC. Otherwise there is a risk of damage to the diamond anvils and other supporting materials, leading to failure of the DAC. Further, various regions of the sample have to be exposed to the focal spot to have uniform heating. In order to achieve the above, nanomotion systems (X–Y Nano) are being used in our LHDAC facility. The DAC is mounted on a XYZ stage, in which motion along the X–Y directions (beam direction: Z) is brought about by two nanomotion systems, with which the DAC can be rastered in steps as small as 10 nm with respect to the focused laser spot.

We have developed a software (AMS-Nanomover) for operating the above nanomotion system using LABVIEW^{TM} (National Instruments Corporation, USA). The requirement to work at safe distances from the high-power laser made us opt for RS-232C interface over the IEEE-488 (cable length restriction ~1–1.5 m only) interface to link the nanomover controller to the PC. The key feature of this software is a front-end virtual joystick, constructed out of a complex network of Boolean 'soft' switches in the back end. This user-friendly software is capable of controlling the X and Y nanomovers simultaneously or separately, as the situation may demand. Additional features include possibility to change the step size from 10 nm up to 2 mm, reading, displaying and saving of X and Y positions of the nanomotion systems on the 'fly', emergency STOP, resetting options and disabling of all motion-control buttons except the one currently under use, etc. Figure 2 gives a flowchart of the nanomover system control software that is self-explanatory.

Imaging system

A simple, cost-effective, remote imaging system was implemented in our set-up by coupling a web-camera to a 100X microscope. This enabled us to achieve good real-time imaging and thereby better focusing of the IR laser beam onto the sample. Further, remote imaging of the hot sample greatly reduces any eye-hazard to the personnel. Recently, we have replaced this with a CCD-based imaging system that offers a higher resolution (640×480 dpi) and maximum magnification of 70X (optical) and 220X (video PC) with a 1.5X objective.

Temperature measurement

Temperature, apart from pressure, is an important parameter that needs to be determined in the LHDAC facility. As the sample volume and the focused IR laser spot size are extremely small in a LHDAC, temperature measurement is a difficult task. Some of the methods that have been reported in the literature are conventional optical pyrometry[9], detailed balance principle exploiting the intensity asymmetry between the Raman Stokes and anti-Stokes lines[15], usage of tiny thermocouples[16] and spectro-radiometry[17]. Among these, the spectroradiometric technique has emerged as the most reliable temperature measurement method suited for the LHDAC[17–19], notwithstanding the fact that temperature gradients in the DAC, chromatic aberrations and unknown wavelength dependence of sample emissivity present limitations on the accuracy. This has been confirmed by recent nuclear resonant inelastic X-ray scattering (NRIXS) experiments of iron samples in a LHDAC[19]. In this NRIXS experiment the principle of detailed balance has been employed, like in Raman spectroscopy, to obtain temperatures from the ratio of the phonon creation and annihilation peak intensities from the NRIXS spectra. The advantage of NRIXS over Raman method is that the nuclear resonance cross-section depends only negligibly on temperature and hence temperature determination is more reliable. Temperatures obtained thus were seen to be closely matching those from
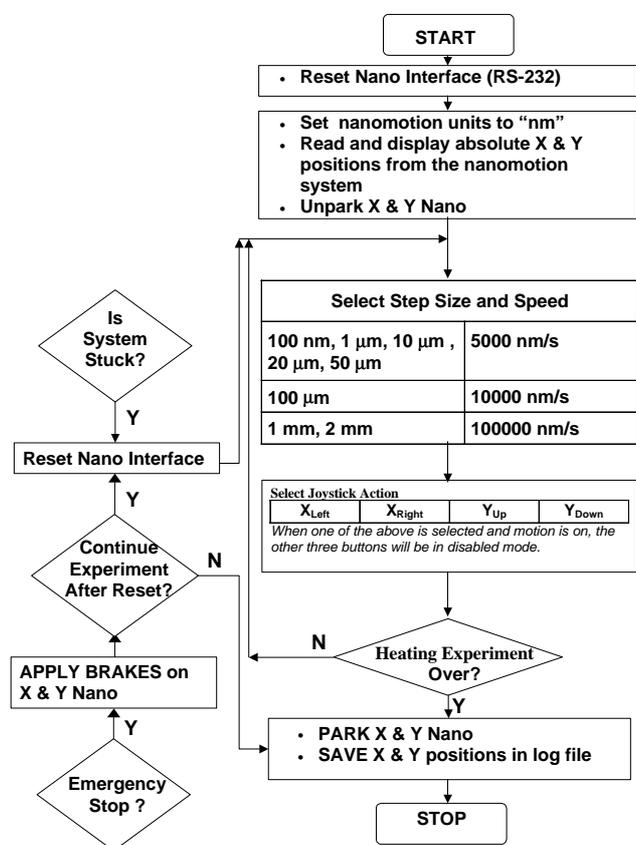

Figure 2. Flowchart depicting nanomover control system logic.

the spectroradiometry method, also employed in the same experiment.

In the spectroradiometry method, the thermal emission spectrum of the hot, microscopic sample in the LHDAC is recorded and the temperature is calculated by fitting it to Planck's function or Wien's function[17]. For our LHDAC facility, we have opted for the spectroradiometry method. The difficulty in temperature measurement lay in focusing the image of the hot and glowing ultra-tiny sample inside the DAC onto an optical fibre tip with 100 μm diameter aperture. We could get over this difficulty and record the thermal spectra of laser-heated samples inside the DAC using a 50F Nikon camera lens and manoeuvring the optical fibre by mounting it onto an x–y–z–q-stage. Signal from the optical fibre is then fed to a CCD-based spectrometer (dual exit and entry ports; focal length 550 mm) shown in Figure 1, for recording the thermal spectrum. This system has been calibrated up to ~3000 K using a 100 W tungsten filament lamp. Figure 3 shows typical thermal emission spectra from a laser-heated graphite sample at two different temperatures and that of the tungsten lamp at ~3000 K. Figure 3 (inset) shows a plot of the thermal emission peak positions of the lamp as a function of its temperature. It is seen to be linear starting from ~1400 up to ~3000 K. The lamp filament temperatures for various voltage settings have been obtained from the known resistance variation with temperature. Temperatures of laser-heated samples could be determined within ~ ± 100 K by recording the thermal emission spectra and using the above calibration curve. This large error bar is common in the LHDAC technique and irrelevant for materials synthesis experiments, such as those being currently done by us. However, for studies related to melting point variation with pressure or determination of P–T phase diagrams, the error in temperature measurement has to be reduced.
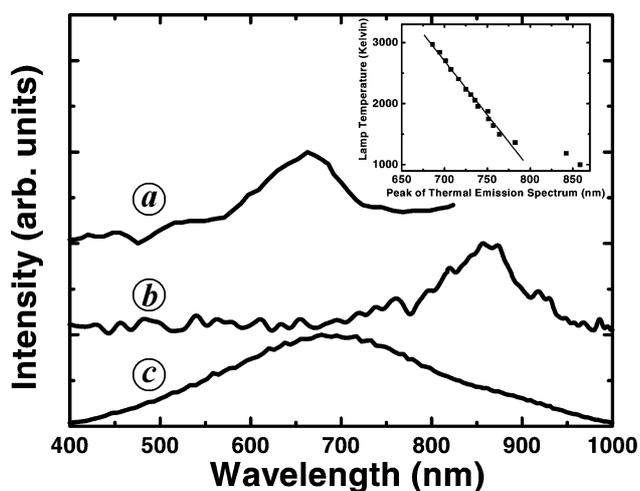
Further calibration of the system beyond 3000 K and more precise determination of the sample temperature is being planned by adopting other strategies like observation of melting of standard materials or use of commercially available temperature calibration standards. These will also enable us to eliminate the spectrometer response contribution from the grey-body spectra, so that they can be fitted to the Planck or Wein's functions and temperature determined more accurately.

Pressure measurement

Pressure measurement using the well-established ruby fluorescence method[20,21] has been accomplished in our LHDAC facility with two options. In the first option, the 5 W argon laser (l = 514.5 nm) is made to travel the same optical path as the heating CO_2 laser and focused onto a small ruby chip placed near the sample inside the DAC. This enables excitement of the ruby fluorescence inside the sample chamber without the need to disturb the DAC aligned for heating. The ruby luminescence spectrum is then recorded using the CCD spectrometer, employing the same optics used for the temperature measurement utility. The second option is a stand-alone-type, where separate optics (not connected to the heating optics) is used to focus the argon laser onto the DAC and collect the ruby luminescence signal. A fibre-optic cable inputs the signal into one of the entry slits of the CCD spectrometer. The other entry slit of the spectrometer is utilized for the temperature measurement part from the LHDAC. Figure 4 shows typical ruby luminescence spectra recorded in our LHDAC set-up at two different pressures. It is pertinent to point out here that in our LHDAC experiments, as we use solid pressure transmitters (NaCl or KBr) that provide a non-hydrostatic environment, the ruby scale is nonlinear even
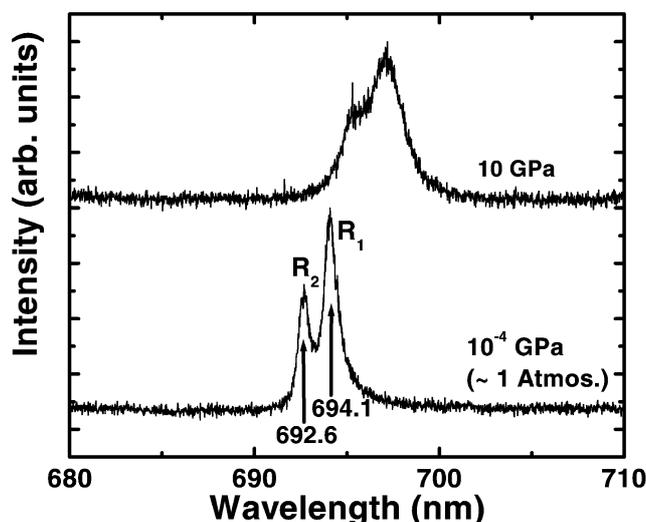

Figure 3. Thermal radiation spectra of a laser-heated graphite sample at ~10 GPa and ~3500 K, (*a*), ~10 GPa and 1100 K (*b*), and that of the tungsten lamp at ~3000 K (*c*). (Inset) Thermal emission peak positions versus filament temperature of tungsten lamp.

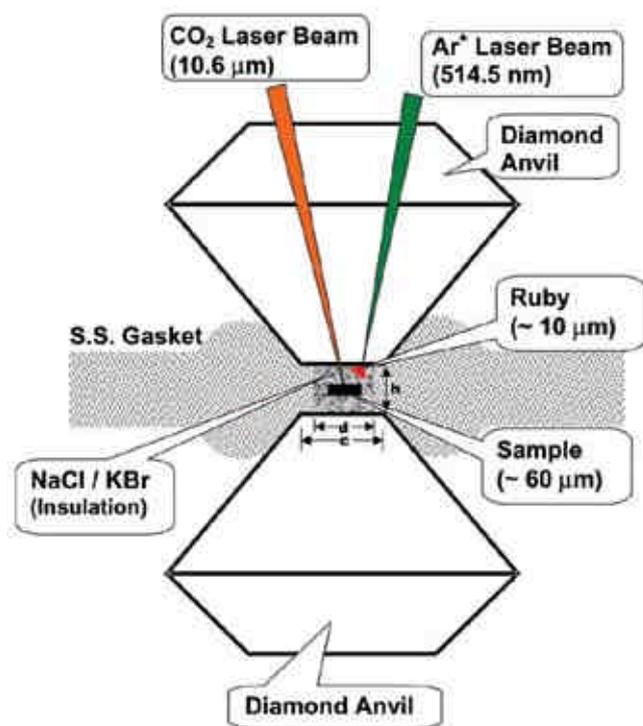**Figure 4.** Ruby luminescence spectra at 10^{-4} GPa (~1 atm) and ~10 GPa.

Figure 5. Schematic of sample chamber for LHDAC experiment. Culet diameter c is ~500 µm; sample chamber is a hole of diameter d ~250 µm and depth h ~80 µm in the ss gasket.

at small pressures. We have used the nonlinear ruby scale[7,20,21] to measure pressure, according to which the pressure P (GPa) is given by

$$P(\text{GPa}) = \frac{1904}{B}\left[\left(1+\frac{dl}{694.24}\right)^{B}-1\right],$$

where dl is the Ruby R_1 line shift in nm. The parameter $B = 5$ for non-hydrostatic conditions and 7.665 for quasi hydrostatic conditions[7].

Synthesis experiments with the LHDAC

With our LHDAC set-up, described in the previous section, we have initiated a few synthesis experiments recently. Some of them have been successful while others have not; however, good experience has been gained in learning the technique, as is exemplified in this section.

The first crucial step is the sample assembly in the DAC and often this decides the course of the high pressure–high temperature heating experiment. Temperatures in the LHDAC set-up can easily go to >5000 K. Since graphitization of diamond takes place at ~900 K, sufficient thermal insulation has to be provided to the diamonds while heating the sample. Additionally, insulation of the sample from the highly heat-conducting diamonds restricts

loss of heat from the sample, thus enabling the achievement of high temperatures[7]. For this purpose, NaCl or KBr are preferred because they act as good thermal insulators, IR windows and also as pressure-transmitting media. Considering these requirements, the sample assembly has been optimized by us as is described below.

Figure 5 shows the schematic of a typical sample chamber assembled for a LHDAC experiment. A stainless steel (ss) gasket is preindented and a hole of diameter ~250 µm and depth of ~80 µm is drilled at the centre. This hole is completely filled with NaCl (or KBr) and is compressed in DAC, so that the NaCl layer becomes transparent. From this region, NaCl is scooped out so as to have a pit of depth ~60 µm, with a radius of ~100 µm. A bottom layer of ~20 µm is left to ensure that the piston diamonds are thermally insulated. Prior to loading in the DAC, finely powdered and mixed starting-species in required stoichiometric ratios is compacted and pelletized between tungsten carbide cylinders in a separate set-up, so as to increase the packing density of the sample. We find that this is important for good absorption of the heating laser beam, which in turn increases the maximum temperature achievable, as well as to obtain a reasonable amount of the reacted product, post-heating, for reliable characterization. A small chip from the pellet of ~60 µm size is loaded into the pit created in the NaCl layer. Above this assembly a thin layer of NaCl is placed, which ensures thermal insulation of the cylinder diamond. A ruby crystal ~10–15 µm diameter is placed in the sample chamber for pressure calibration.

The first experiment we carried out in order to demonstrate successful setting-up of our facility was the well-known problem of direct conversion of graphite to a transparent phase[22,23]. A high-purity graphite chip (linear dimension ~75 µm) was loaded in the DAC in the manner described above and the CO_2 laser focused onto it. We found that at a pressure of ~15 GPa and at a laser power of ~15 W, exothermic reaction characterized by flashes of bright light got initiated. The temperature was estimated to be ~2000 K. Using the nanomovers, we rastered the sample across the CO_2 laser beam. Images of the graphite sample prior to laser-heating, during heating and after ~45 min of heating are shown in Figure 6. The pressure on the sample was ~15 GPa. In Figure 6 a, the graphite sample is seen as a black or dark-grey chunk in the middle of the 250 µm diameter sample chamber, that has been illuminated by light from the back side, and viewed from the front side (i.e. in the light transmission mode). The bright region around the black graphite sample is the transmitted light coming through the NaCl. After the heating event lasting for nearly 45 min, we found that the entire graphite chip had become translucent to light (i.e. not fully transparent) under this same illumination arrangement. This is seen in Figure 6 c. Subsequent to this transformation, the sample totally stopped absorbing the laser wavelength. The transparent phase was found to remain so after temperature

Figure 6. Heating of graphite with the LHDAC set-up at $P \sim 14$ GPa: (*a*) before heating, (*b*) during heating with CO_2 laser and (*c*) after heating (Webcam pictures).
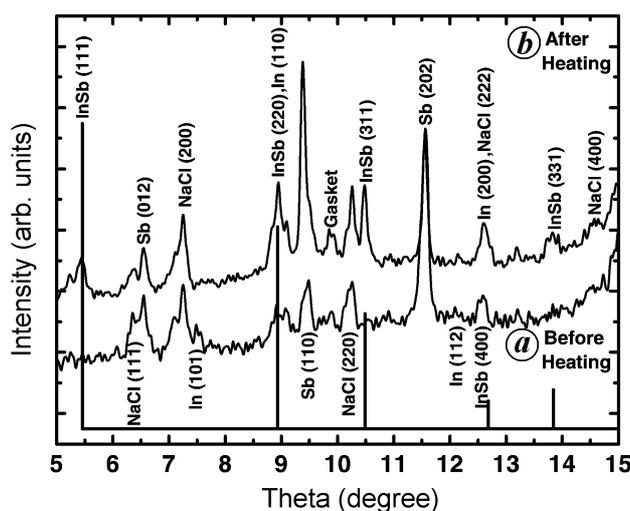

Figure 7. Direct elemental synthesis of InSb by laser-heating a mixture of In and Sb at high pressure. (*a*) Mixture before heating, (*b*) after heating: Occurrence of (111), (220) and (311) peaks of zincblende InSb can be clearly seen. Graphical representation of positions and peak intensities from the standard powder XRD data file of InSb[26] has also been shown for comparison.

and pressure quenching. The DAC was examined thoroughly after the experiment. We did not find any damage to the cell and its constituents.

Next, we tried the synthesis of boron arsenide (BAs), a strongly covalent III–V compound. The LHDAC was used for the twin purpose of confining the boron and the highly subliming arsenic as well as to induce direct elemental reaction between them at high temperature and modest pressures of a few GPa. At various pressures the sample, rastered by nanomovers, was heated with the CO_2 laser. Flashes of light corresponding to absorption of the laser wavelength could be seen and maximum temperatures reached were ~1800–2000 K. The temperature-quenched sample was characterized using our High-Pressure Guinier X-Ray Diffraction set-up, described in detail by Sahu *et al.*[24], at each pressure step following the heating event for phase formation. We observed under increasing pressures that the CO_2 laser wavelength of 10.6 μm was increasingly not able to couple with the sample and beyond

~5 GPa, there were no flashes or visible hot-spots. Mild heating of the DAC metal parts was however detected. Actually, under application of pressure, absorptivity of the sample changes and it may exhibit decreasing absorption of the laser wavelength as pressure is increased (i.e. the input laser power may have to be increased as pressure is increased, to achieve the same heating), as is the case in the present experiment. The unabsorbed fraction of the incident IR laser light gets scattered from the sample and leads to mild heating of the surrounding metal regions.

Nevertheless, we continued the experiments up to ~10 GPa. High pressure X-ray diffraction (XRD) patterns showed that all the parent phase lines were present; but for some redistribution in the line intensities, there was no clear indication of BAs compound formation.

The next experiment was an attempt to reproduce synthesis of another III–V compound, namely indium antimonide (InSb) with the LHDAC set-up. The elements In and Sb in powder form were loaded in the DAC and heated with

the CO_2 laser. Heating experiments were done up to ~2.5 GPa and ~2000 K. Figure 7 shows the XRD patterns of the sample at ~0.5 GPa, before and after heating. Appearance of the distinct (111), (220) and (311) peaks of zincblende InSb[25] can be noticed after laser-heating. Graphical representation of the positions and peak intensities from the standard powder XRD data file of InSb[26] has been shown for comparison.

This successful synthesis experiment gave us confidence to explore synthesis of a variety of novel rare-earth metal carbides, which can exhibit high elastic modulii, by directly reacting rare-earth elements with carbon at high pressures and high temperatures. The idea was that even though the rare-earth metal may not be a good absorber of 10.6 μm radiation from the CO_2 laser, the carbon will effectively absorb it and get heated. This heat should provide sufficient kinetics for the reaction between the rare-earth metal and carbon. Ruthenium carbide (RuC) was the first one to be tried[27]. We found that even up to ~12 GPa, there was no indication of compound formation in the XRD patterns, even though bright thermal flashes indicating exothermic reaction were seen. We observed that at increasing pressure, absorption of the CO_2 laser wavelength by the sample decreases, leading to inefficient heating. It remains to be seen whether heating the system with a Nd : YAG laser (1.06 μm) will be more efficient, as this wavelength is known to be well suited for metallic systems. This laser (30 W, 1.06 μm, CW, TEM_{00} mode) is in the process of being integrated into the LHDAC facility at present.

During the course of the heating experiments, discussed in the previous paragraphs, we rastered the sample with the heating laser beam continuously for even up to 3 h. Careful inspection of the DAC showed that the cell or its constituents had not suffered any damage. This demonstrated the high level of perfection in the optics that has been designed and set up by us.

To summarize, we have set up a LHDAC facility to investigate materials behaviour at very high pressures and temperatures. The present set-up will be utilized chiefly to study insulating samples in view of their efficient absorption of the 10.6 μm radiation of the CO_2 laser. Our immediate target will be to attempt high pressure–high temperature synthesis of superhard materials involving low Z elements such as C, N, B, Li, etc. and also synthesis of carbides, nitrides and oxides of the transition metals. The samples synthesized in the LHDAC are being characterized for their structure by XRD after quenching the temperature, but with the sample still locked under desired pressure in the DAC. This method can be expected to be most successful, if the synthesized phase remains stable after temperature quenching. Alternatively, on-line *in situ* structural characterization of the samples even while the heating event is going on, can be done if a similar LHDAC facility is set up on an X-ray synchrotron beamline (like INDUS-II), as is being done by a few contemporary

groups in other countries. Another on-line characterization tool is Raman spectroscopy, which we are in the process of setting-up, by installing a holographic notch filter in the pressure–temperature measurement optics already being used in the LHDAC set-up. The present LHDAC system is of single-sided heating-type, and uniform heating of the sample is being achieved to some extent by rastering the sample slowly with the nanomovers for a given laser power. This will minimize the effects due to radial temperature gradient. Also, multi-mode operation of the laser (Nd : YAG) can make it spatially wider compared to the single-mode operation and thereby minimize radial temperature gradient[28]. The price to be paid will be in the form of lower power density and lesser stability compared to the single-mode operation. However, to minimize the effects due to axial temperature gradient, it would be better to heat the sample from both sides along the beam-axis. The LHDAC set-up presents itself for easy adaptability for this double-sided heating arrangement.

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