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TOPICAL REVIEW — Synergetic Extreme Condition User Facility: Breakthroughs and opportunities for the research of physical science

Function of large-volume high-pressure apparatus at SECUF

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Pressure allows the precise tuning of a fundamental parameter, the interatomic distance, which controls the electronic structure and virtually all interatomic interactions that determine material properties. Hence, pressure tuning is an effective tool in the search for new materials with enhanced properties. To realize pressure tuning on matter, large-volume press (LVP) apparatuses have been widely used not only to synthesize novel materials but also to implement the *in situ* measurement of physical properties. Herein, we introduce the LVP apparatuses, including belt-type, cubic anvil, and 6–8 type multi-anvil, that will be constructed at the Synergetic Extreme Condition User Facility (SECUF) at Jilin University. Typically, cell volumes of 1000 mm^3 can be obtained at 20 GPa in a belt-type apparatus that is significantly larger than that obtained in a 6–8 type multi-anvil apparatus at the same pressure. Furthermore, the *in situ* measurement of physical properties, including thermological, electrical, and mechanical behaviors, is coupled to these LVP apparatuses. Some typical results of both synthetic experiments and *in situ* measurements obtained from the LVP apparatuses are also reviewed.

Keywords: high pressure, large-volume press, multi-anvil apparatus, *in situ* measurement, synthesis

PACS: 61.50.Ah, 62.20.Qp, 91.60.Ed, 91.60.Gf **DOI:** 10.1088/1674-1056/27/7/076103

1. Background

It is well known that high pressure can have a very large effect on the chemical and physical properties of matter, and it is a thermodynamic variable as fundamental as temperature.[1] Under high pressure, large changes in the density, electron configuration, and free energy will occur.[2] In particular, chemical equilibria and material properties will undergo extreme alterations, resulting in a wide range of new compounds and unusual states of matter. Thus, pressure is a useful tool both for the synthesis of new matter and for probing existing phases of scientific or technological significance. For example, it has been confirmed that the metal sodium (Na) is transformed into an insulator under 200 GPa.[3] Although considerable attention has been paid for the preparation of metastable materials, because many of the most interesting and useful materials are metastable, there are few effective methods. Many metastable materials can be synthesized at high pressure and quenched to ambient conditions whilst remaining kinetically stable.[1] Moreover, with the development of high-pressure technology, the properties induced under pressure can be *in situ* probed and optimized as a function of a fundamental parameter: interatomic distance.[4] The information gained from pressure-tuning studies is invaluable in the search for and design of new materials that may be synthesized at ambient pressure.

To carry out pressure tuning, a high-pressure apparatus is necessary. Static pressures as high as 400 GPa are now achievable inside a diamond anvil cell (DAC). However, the sample obtained in a DAC is too small to characterize when the pressure is released. Compared to a DAC, the sample volume in a large-volume press (LVP) apparatus is large, and it can vary between the mm^3 and cm^3 scales. This is very important for subsequent analysis of the quenched sample under ambient conditions. Over the past few years, LVP apparatuses in a number of different configurations that generate pressures in the range 3–28 GPa while simultaneously heating to temperatures up to 3000 K[5] have been used both in synthesis experiments and for *in situ* measurements. Recently, these LVP apparatuses have become widely used in the fields of deep-Earth science, physics, and materials.

Herein, we introduce the LVP apparatuses that will be constructed at the Synergetic Extreme Condition User Facility (SECUF) in Jilin University. The anvils for these LVP apparatuses include belt-type, Walker-type, Kawai-type, and DIA-type. The LVP apparatus can be used not only for synthesis experiments but also for *in situ* measurements of physical properties including thermal diffusivity, electrical conductivity, and elastic properties via ultrasonic measurements.

2. Introduction to LVP apparatuses

In general, the high-pressure cells of LVP apparatuses can be divided into belt-type, cubic, and octahedral volumes. Pressures of $\sim$ 10 GPa can be generated in belt-type apparatus cells.[6] Although the cell pressure is not high, the volume of the sample in a belt-type cell is large. The hinge-type cubic anvil apparatus has been widely applied in scientific and

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technologic fields in China, in particular, to produce superhard materials for industrial applications.[7] The largest velocity of boosting and decompressing pressure can be obtained in this type of apparatus. In general, cell pressures of typically 6 GPa and cell volumes of 425 cm^3 can be generated in CS-XII type cells. Within this class of apparatuses, the octahedral-anvil apparatus is one of the most popular high-pressure apparatuses, with a cell pressure of 28 GPa.[8] This is a type of multi-anvil apparatus (MAA), which is characterized by the 6–8 type double-stage compression such that an octahedral pressure medium is squeezed by truncated corners of eight cubic anvils which are compressed by six outer anvils. The first-stage anvils are Walker-type and Kawai-type, respectively in MAA. Furthermore, another LVP apparatus is a DIA-type guide block system which has been installed at a beam line station for *in situ* x-ray observation.[9]

It is very important for high-pressure science that an LVP apparatus can generate a high cell pressure whilst maintaining a large sample volume. In recent years, at room temperature, a pressure of 64 GPa, which is the highest pressure ever generated with a Kawai type multi-anvil apparatus (KMA) using tungsten carbide (WC) anvils, was achieved using 1°-tapered anvils with a 1.5-mm truncation.[10] When sintered diamond was used as the second anvil, pressures of 80–90 GPa were generated.[11] Furthermore, a new 6-axis apparatus in which the movements of the six anvils are controlled by a servo mechanism is very advantageous for the generation of higher pressures in the Kawai-cell.[12] Large sample volumes, however, are essential not only in synthesis experiments for subsequent characterization under ambient conditions, but also for many *in situ* physical property measurements. The *in situ* measurements often require more than one wire, which is also facilitated by using a large sample assembly.[13,14] In order to enlarge the sample volume, the capacity of the hydraulic press to push the anvils is often enhanced. For example, anvils are compressed using a hydraulic press with a 6000 t (60 MN) and 5000 t (50 MN) capacity constructed at Ehime university in Japan[15] and at Bayerisches Geoinstitut (BGI) in Germany,[5] respectively. Moreover, a larger cell volume may be generated in a hinge-type cubic anvil with a 6–8 second-stage anvil, as developed by He at Sichuan University.[16] Because the hydraulic pressure generated in the hinge-type apparatus is much larger than that in the double-stage MA apparatus.

Although the 6–8 type double-stage MAA is one of the most popular LVP apparatus for high pressure science, the sample volume is lower than that of the belt-type apparatus. Unfortunately, pressures obtained in belt-type apparatuses are lower than 10 GPa, which limits their application. It is very important to increase the cell pressure obtained in belt-type apparatuses while maintaining the larger sample volumes. Therefore, as user facilities, many kinds of LVP apparatuses, including the popular 6–8 type double-stage apparatus and belt-type anvil apparatuses, will be constructed at SECUF at Jilin University to meet the needs of users (shown in Fig. 1). Moreover, a new belt-type apparatus with enhanced cell pressure has been designed. The enhanced cell pressure, 20 GPa, can be realized by the pressure gradient designation for the gasket with prestressing force. The schematic diagram of this apparatus is shown in Fig. 2.

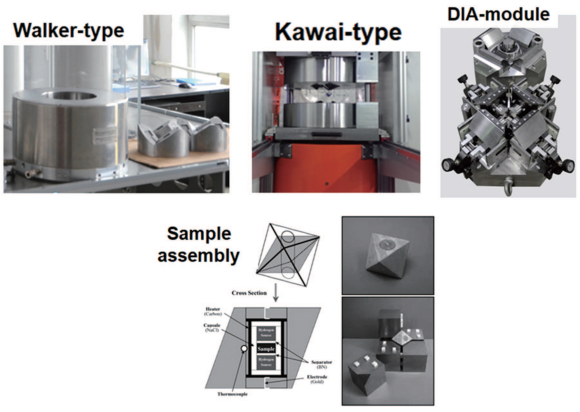


Fig. 1. (color online) The 6–8 type double-stage apparatus designs.

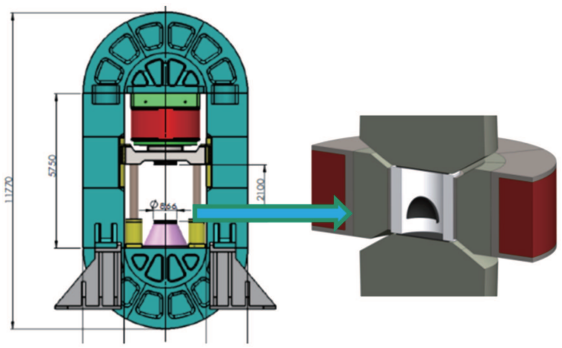


Fig. 2. (color online) Belt-type apparatus design.

3. Function of LVP apparatuses

LVP apparatuses are necessary devices for carrying out pressure-tuning research studies. In general, the function of the LVP includes both synthesis experiments and *in situ* measurements, and has been widely applied in the fields of deep-Earth science, physics, and materials. It is very important to develop *in situ* measurement techniques with LVPs constructed at synchrotron radiation facilities offline. Here, some typical results of both synthetic experiments and *in situ* measurements obtained from the LVP apparatus in our lab will also be reviewed. These results confirm that the LVP being constructed at SECUF at Jilin University can supply the above function for users.

3.1. Synthetic experiment

Most metastable materials with remarkable properties can be obtained at high pressure and high temperature. Synthetic

diamond, as a typical superhard material, is transformed from carbon at high pressure and high temperature and has been widely used in many fields. Since synthetic diamond was reported in the 1950 s, there has been much progress in this field concomitant with the development of LVP apparatuses.[17] Recently, nano-polycrystalline diamond (NPD), which is superior to diamond, has been prepared from a nanocarbon source.[18] Furthermore, nanotwinned diamond (NtD), was successfully synthesized in a multi-anvil high-pressure apparatus, under high pressure and high temperature (HPHT) conditions, using carbon onion precursors.[19] The Vickers hardness of high quality NtD with an average twin thickness of 6.8 nm reached as high as 180 GPa (shown in Fig. 3).[20] This value is much larger than the 200 GPa value reported by Tian.[19]

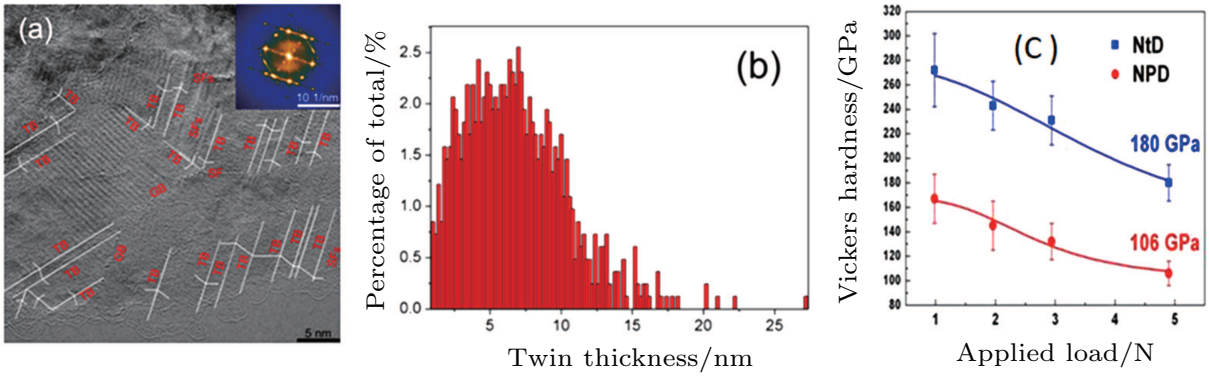


Fig. 3. (color online) (a) High resolution transmission electron microscope (HRTEM) image of NtD synthesized from carbon onions (2000 °C, 20 GPa), the insert pattern is a selected area electron diffraction (SAED) result. Twin boundaries (TB) are each marked by a long white line with two short lines either side; the two short lines indicate the direction of the lattice fringes. Twins are terminated at grain boundaries (GB). Stacking faults are found in the lattice, which are marked as SF and SFs. (b) The twin thickness distribution, as obtained by measuring the distance of two long white lines. A total of 823 twins were measured to acquire this twin thickness distribution. (c) Vickers hardness of NtD and NPD.[20]

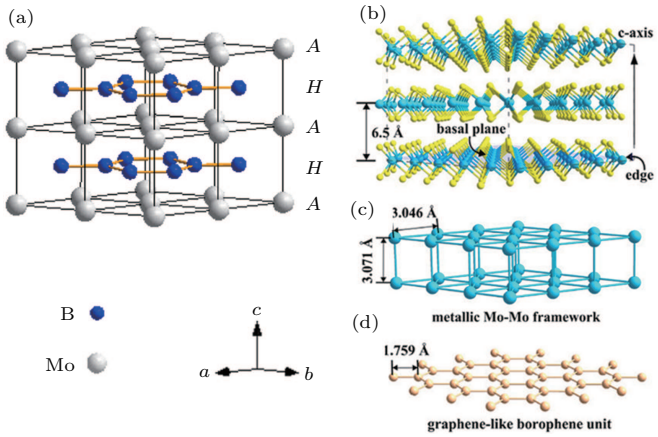


Fig. 4. (color online) Crystal structures of α-MoB_2 and MoS_2. Large white spheres represent Mo atoms, small blue spheres are B atoms. (a) α-MoB_2 ($P6/mmm$) structure with AH stacking sequence. (b) Crystal structure of MoS_2. (c) Three-dimensional metallic Mo–Mo framework in α-MoB_2. (d) Two-dimensional graphene-like borophene units in α-MoB_2.

In another example, the metastable material alfa-phase molybdenum boride, α-MoB_2, was successfully synthesized from boron and molybdenum powders at HPHT.[21] α-MoB_2 has $P6/mmm$ structure which is similar to MoS_2 (Fig. 4(b)), and the stacking is formed by only two kinds of layers alternately arranged, AH (Fig. 4(a)), where H is a flat boron six-ring network layer, like graphene, and A represents the molybdenum layer, in which Mo atoms occupy positions above and below the center of the boron ring. The Mo atoms in α-MoB_2 are metallically bonded to form 3D frameworks (Fig. 4(c)), whereas the B atoms are covalently bonded into unusual 2D graphene-like borophene structures (Fig. 4(d)) that do not exist in the isolated form. The structure of α-MoB_2 can, thus, be viewed as an interconnected, sandwich-like configuration comprising borophene-inserted Mo-based 3D frameworks.

The results of a hydrogen evolution reaction (HER) identify α-MoB_2 as an active and stable electrocatalyst for HER.[22] In contrast to MoS_2, α-MoB_2 is a nonlayered, three-dimensional material that possesses metallic properties and high electrical conductivity as well being rich in catalytic active sites (because not only its "edges", as in MoS_2, possess the catalytically active sites). This is among the reasons why α-MoB_2 affords a high current density of 1000 mA/cm^2 during HER at a small overpotantial.[22]

3.2. *In situ* measurement

It is very important to develop *in situ* measurement capacity at HPHT for effective probing of pressure tuning on matter. For example, the elastic bulk and shear moduli as well as their pressure dependences are important parameters for understanding the structural behavior and physical or mechanical properties of materials. These properties can be obtained by *in situ* measurement experiments at HPHT, for example, via the ultrasonic interferometric measurements developed by Li.[23]

Transition-metal nitrides have recently attracted considerable interest in condensed matter physics, solid-state chemistry, and materials. We have measured the ultra-

incompressibility and high shear rigidity of polycrystalline hexagonal ε-NbN using ultrasonic interferometry at HPHT.[24] Using a finite strain equation of state approach, the elastic bulk and shear moduli, as well as their pressure dependences, are derived from the measured velocities and densities, yielding $B_{S0} = 373.3(15)$ GPa, $G = 200.5(8)$ GPa, $\partial B_S/\partial P = 3.81(3)$, and $\partial G/\partial P = 1.67(1)$ (the number in parentheses is the measurement error for each measurement). Hexagonal ε-NbN possesses a very high bulk modulus, rivaling that of the superhard material cBN ($B = 381.1$ GPa); its high shear rigidity is comparable to that of the superhard γ-B ($G = 227.2$ GPa).[24]

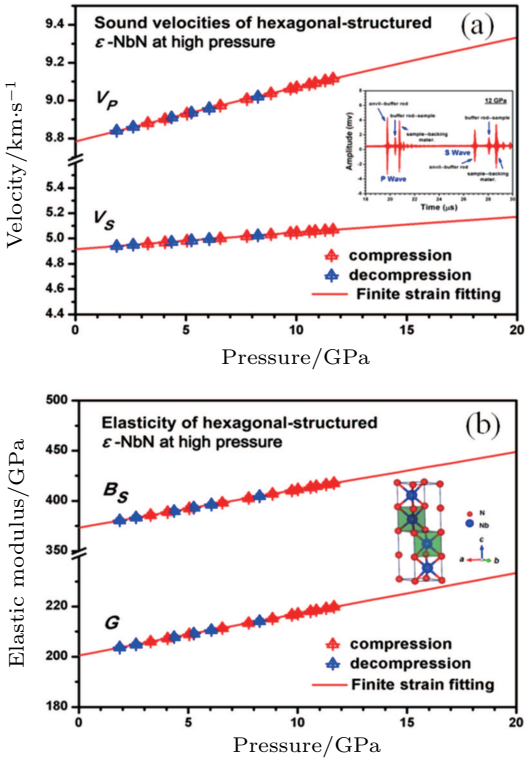


Fig. 5. (color online) (color online) (a) Elastic wave velocities (V_P and V_S) of polycrystalline hexagonal ε-NbN at high pressure; a representative acoustic echo of the ultrasonic measurements at the highest pressure, $\sim$ 12 GPa, is shown in the inset. (b) Elastic bulk and shear moduli (B_S and G) of polycrystalline hexagonal ε-NbN at high pressure. Red circles denote velocities upon compression, and blue solid circles those during decompression; red solid lines are from third-order finite strain fits. Figure adapted with permission from Ref. [24].

Furthermore, we developed a method for performing simultaneous measurements of the electrical resistivity and the Seebeck coefficient at HPHT in a cubic multi-anvil apparatus.[25] For *in situ* measurements at HPHT, a four-probe arrangement is used to measure the electrical resistivity and two pairs of chromel-alumel type thermocouples are employed to determine the Seebeck coefficient (Fig. 6). The results demonstrated an expected temperature-induced phase transition, pressure-induced metallization, and enhancement of the thermoelectric properties in Ag_2Te (Fig. 7).[25]

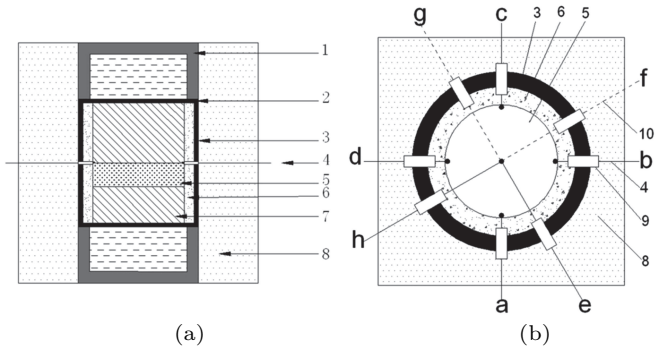


Fig. 6. Schematic illustration of a cell assembly. (a) Longitudinal section of the cell assembly: (1) steel ring, (2), (3) graphite heater resistance, (4) Pt electrode (a, b, c, and d in (b)), (5) sample, (6), (7) MgO insulation material, (8) pyrophyllite. (b) Cross section of the cell assembly: (9) Al_2O_3 tube insulation material, (10) chromel-alumel type thermocouple (e, f, g, and h). Figure adapted with permission from Ref. [25].

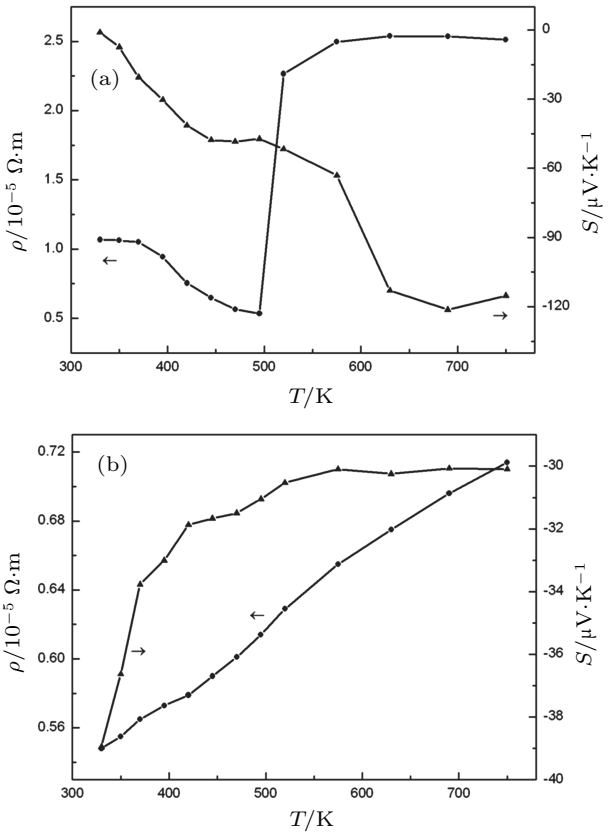


Fig. 7. Temperature dependence of the electrical resistivity and Seebeck coefficients of Ag_2Te at selected pressures of (a) 2.0 GPa and (b) 5.2 GPa. Figure adapted with permission from Ref. [25].

Another *in situ* measurement method, high-pressure differential thermal analysis (HPDTA), was developed by He.[26,27] Differential thermal analysis (DTA) is one of the direct methods for studying the thermodynamics of phase segregation. HPDTA is very useful for detecting the phase decomposition temperature and thermal stability of materials under high pressure. Usually, two thermocouples are brought into the samples and the differential voltage versus sample thermocouple voltage is recorded.[25] With this method, two temperature-induced phase transitions in $Na_{0.5}Bi_{0.5}TiO_3$

(NBT) were observed at around 220 °C and 520 °C, below 0.7 GPa.[26] Measured phase decomposition temperatures of Ti_2AlC were 890 ± 10 °C at 5 GPa and 1030 ± 10 °C at 4 GPa.[27]

4. Summary and outlook

The LVP apparatuses that will be constructed at SECUF, including belt-type, 6–8 two-stage type, and DIA modules, can be used not only for synthetic experiments but also for *in situ* measurements of physical properties. It is noted that a cell pressure of 20 GPa has been designed for a belt-type apparatus, which is significantly higher than that of the traditional belt-type apparatuses and the popular MAA apparatus. The sample volume obtained from a belt-type apparatus is considerably larger than that from MAA apparatuses at the same pressure. The cell pressure obtained in a belt-type apparatus can be increased when another module is used. Furthermore, based on the developed in situ measurement technologies, physical properties including thermological, electrical, and mechanical behaviors can be obtained at a pressure of 28 GPa and a temperature of 2500 K. The LVP apparatus constructed at SECUF will serve as a multiple-function user facility for high-pressure science.

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Dedicated to Prof. Guangtian Zou on the occasion of his 80th birthday.

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