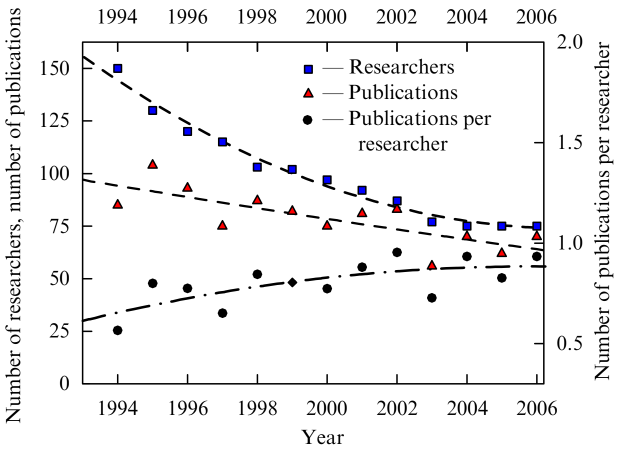

Figure 11. Variation of the number of researchers and number of scientific reports at the IHPP.

At present, the proportion of fundamental research is increasing noticeably at the institute. Although high-pressure materials science and the development of apparatuses remain among the main scientific focuses of the institute, the emphasis in investigations has shifted toward the fundamental problems of the physics of condensed matter, including phase transitions at high pressures, quantum critical phenomena and strongly correlated electron systems, the thermodynamics and kinetics of phase transitions in disordered systems, and the physics of nanosized forms of carbon.

Unfortunately, the institute is not free of the problems that are common to all academic institutions. In the last 15 years, the number of workers at the institute has decreased by a factor of more than three. Figure 11 displays the dynamics of the changes in the number of researchers at the institute, the total number of publications per year, and the number of publications per researcher per year. A certain optimism comes from the fact that, as is seen from the figure, the number of publications per researcher has increased quite noticeably. However, the fraction of young researchers remains insufficient, in spite of the existence of a base chair in the Moscow Physico-Technical Institute (The Physics of Condensed Matter under Extreme Conditions) and of academic postgraduate courses, as well as of intimate cooperation with the Moscow Institute of Steel and Alloys and the Departments of Physics and Chemistry at Moscow State University.

PACS numbers: **01.65.+g**, **07.35.+k**, 64.70.kd
DOI: 10.1070/PU2008v051n10ABEH006615

Large-volume high-pressure devices for physical investigations

L G Khvostantsev, V N Slesarev

In this report, we briefly describe the development of domestic high-pressure engineering (above 5 GPa) in large volumes for physical investigations. We give the technical characteristics of the high-pressure cells of the 'toroid' and 'chechevitsa' (lentil) types invented at the institute and show their experimental potential in studying the structure and properties of condensed matter. We describe a number of examples of studying solids and liquids by various methods using these devices. The possibility of efficient application of the lentil and toroid cells in industry for the synthesis of superhard materials is noted.

High-pressure physics deals with studying a large totality of phenomena in condensed matter under high compression. As the density of solids and liquids increases, noticeable changes in their physical properties, their crystal and electronic structures, and the mutual arrangement of atoms in them are observed. Studying these phenomena, especially in combination with low and high temperatures and magnetic fields, yields valuable information necessary for the further development of concepts of the structure of condensed matter. On the other hand, this information is important for solving the main problem of materials science — preparation of new materials with unique properties — which is related to the synthesis of high-pressure phases that are formed as a result of irreversible polymorphic transformations.

The choice of phenomena to be studied is determined by the capabilities of the high-pressure equipment. High-pressure cells are characterized by the ranges of working pressures and temperatures and by the magnitude of the working volume. Large volumes are necessary for obtaining more complete and reliable information, since in cells with a large volume homogeneous pressure and temperature fields can be produced, samples of a desired size can be used, and various sensors, including pressure and temperature gages, as well as heaters, thermal isolation, and coils for generation of magnetic fields, can easily be mounted.

To produce high pressures reaching thousands and tens of thousands of atmospheres, two types of high-pressure devices have been used from the beginning of the 20th century, namely, the piston – cylinder apparatus and Bridgman anvils (Fig. 1) [1, 2]. In apparatuses of both types the pressure is created due to a decrease in the volume of the substance to be pressed. In the piston – cylinder cell the compression of the substance can be any size: the production of maximum pressures is limited by the strength of the construction materials. Devices of this type make it possible to perform investigations in large volumes ($1-100$ cm^{-3} and greater) at pressures that are, as a rule, no more than $3-5$ GPa. In the apparatus of the anvil type, Bridgman used the principle of a compressed seal, which consists in the fact that a thin gasket placed in the gap between approaching parts of the apparatus can keep the high pressure created in the working volume. Since the gasket (compressed seal) unavoidably has a small thickness, the volume of the compressed substance is also small. The anvils, made of a hard alloy, make it possible to easily reach pressures of more than 10 GPa, but only in very small volumes of $10^{-2}-10^{-3}$ cm^3 at a sample thickness of ~ 0.1 mm.

The problems of physics, geophysics, and materials science, the most important of which was the problem of synthesizing artificial diamonds, required the development of cells of a larger volume (0.1 cm^3 and greater) capable of sustaining high pressures (> 5 GPa) and temperatures ($> 1500\,^\circ$C) for long periods. These problems were solved in different ways, which finally led to the development of numerous devices of various constructions, combining (in various proportions) ideas that were laid in the initial variants, i.e., in the apparatuses of the anvil and piston – cylinder types.

In the West, apparatuses of two main types, namely, of the belt type and multianvil type, have been developed (see Fig. 1)

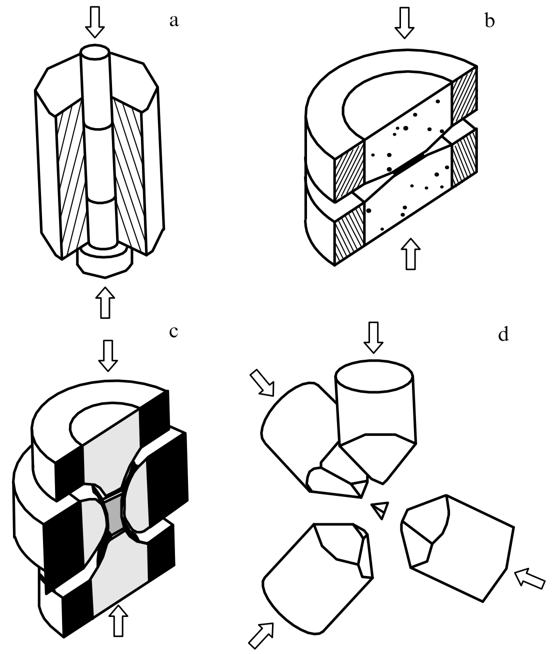

Figure 1. Main types of foreign high-pressure cells: (a) piston – cylinder; (b) Bridgman anvils; (c) belt: and (d) multianvil cell.

[1, 2]. It is using the belt-type cell that artificial diamonds were synthesized for the first time at the General Electric Company. Cells of both types made it possible to reach pressures above 6 GPa (8 – 10 GPa at present); in the United States, Europe, and Japan they are now the basic apparatuses for synthesizing superhard materials and are employed for physical and geophysical investigations. At present, multistage devices based on the belt-type apparatuses and multianvil cells with the use of elements made of diamond or cubic boron nitride at the final stage make it possible to reach pressures of 20 – 30 GPa in relatively large volumes (~ 10 mm^3). Apparatuses of the piston – cylinder and Bridgman-anvils types have also diligently been perfected. Thus, the piston – cylinder cell with an all-round support make it possible to achieve pressures to 5 – 7 GPa in a volume of ~ 10 cm^3 [3]. The creation of cells with anvils made of diamond and the employment of gaskets made of high-strength metals and alloys made it possible to reach pressures as high as 300 GPa; investigations at pressures around 100 GPa are at present routine problems. However, the volumes that can be processed in diamond anvil cells are very small (10^{-6} to 10^{-9} cm^3).

In Russia, cells of the toroid and lentil type have been successfully employed for scientific investigations for more than 40 years; because of their unusual construction, they have not been used for a long time in other countries [4]. The designing of chambers of a large volume for creating pressures exceeding 5 GPa in Russia was based on the idea used in Bridgman anvils.

Work on designing high-pressure apparatuses of large volume at the Institute for High Pressure Physics, Russian Academy of Sciences, (IHPP) were initiated in 1958 in connection with the objective of synthesizing diamond and cubic boron nitride taken on by the institute. When studying the method of Bridgman anvils, the idea arose that the compressed sealing gasket can efficiently work in the case of compression not only by parallel planes but also by diverging surfaces. This makes it possible to construct a high-pressure cell of large volume using the principle of the compressed seal. The approach of the cell elements necessary for compressing a large volume can be provided by creating negative pressure gradients in this volume from the center to the periphery. These ideas were used as the basis for constructing a cell of the lentil type, in which a ring seal with an approximately conical profile of a ring cross section reliably maintains pressure in a lentil-like cavity of the high-pressure cell. After a thorough study of the mechanism of the functioning of the chamber, a construction was designed that permitted one to reliably reach pressures of more than 8 GPa at temperatures of up to 2300 K, which can be maintained for a long time (Fig. 2). In this way, the parameters required for the synthesis of diamond and cubic boron nitride were reached [5, 6]. The creation of a lentil-type cell was in fact a breakthrough into a new range of pressures and temperatures in domestic science and engineering. In 1960 the lentil-type setup was used at the IHPP to synthesize diamond and cubic boron nitride for the first time in the Soviet Union. Cells of this type had working parameters (pressure and temperature) close to those characteristic of the belt-type cell; however, they were much cheaper and much simpler to handle than apparatuses from the West. A powerful diamond industry developed in the Soviet Union and Comecon (Council for Economic Assistance) countries, mainly based on the employment of just this type of high-pressure cell. The lentil-type cell is still used in industry for the synthesis of abrasive powders based on diamond, cubic boron nitride, and composite superhard materials.

Using the lentil-type cell, for the first time in the world combinations of pressures of more than 9 GPa and tempera-

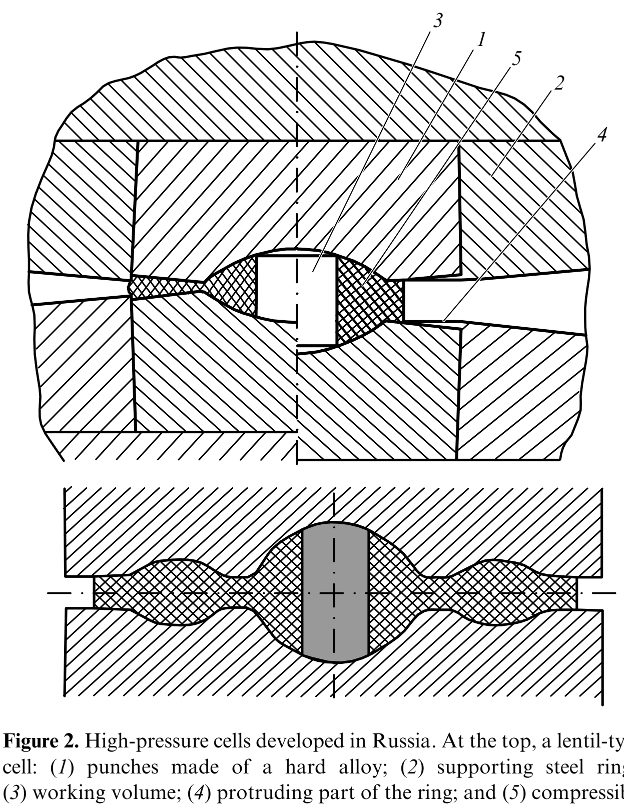

Figure 2. High-pressure cells developed in Russia. At the top, a lentil-type cell: (*1*) punches made of a hard alloy; (*2*) supporting steel rings; (*3*) working volume; (*4*) protruding part of the ring; and (*5*) compressible seal made of a lithographic stone (on the right, the initial position; on the left, the working position). At the bottom, a toroid-type chamber; the parts and the materials are analogous.

tures of 1500 °C necessary for the synthesis of the dense phase of silica (stishovite) in large volumes were obtained [7]. The discovery of stishovite made it possible to obtain a consistent model of the lower mantle of the Earth. The role of phase transitions in the formation of the structure of the Earth and other planets was thus experimentally shown. This discovery is one of the most important contributions to the development of the Earth sciences.

There are a number of designs of the lentil-type cell with different volumes (with the diameters of the hole from 15 to 50 mm). In 1963 the IHPP in cooperation with which industry designed a cell with a record large volume of ~ 200 cm^3 (diameter of the hole ~ 100 mm) and with a high-temperature zone of ~ 60 cm^3 operative at pressures of up to ~ 6 GPa and temperatures of ~ 1900 K (Fig. 3) [8]. The synthesis of abrasive diamonds carried out in this cell gave an output of ~ 24 g per cycle.

The following step in the development of high-pressure devices of large volume was the invention at the IHPP of a cell of the toroid type [9], whose construction is a logical continuation of the idea of the lentil-type cell (see Fig. 2). What distinguishes the toroid-type cell from the previous designs is the presence of a toroidal depression around the central part of the working surface of the punches. The pressure that is generated in the region of toroidal depression fulfills two functions. First, it sharply decreases the extrusion of the central part of the gasket. Even at maximum pressures, the clearance between the anvils remains sufficiently large, permitting the introduction of a large number of measuring wires. On the other hand, the pressure in the toroidal depression reduces the value of shear stress in the punch, which leads to an increase in the ultimate pressures and in the mechanical reserve of the cell. The ultimate pressure in the toroid-type cell (just as in the lentil-type cell) depends on the working volume. The values of the ultimate pressures in the toroid-type cells made from a high-quality hard alloy are given in the table, depending on the diameter of the central hole.

The values given in the table exceed the appropriate pressures accessible in apparatuses of the belt type and in the multianvil cells of comparable working volumes. Recently, a design was developed on the basis of the toroid-15 cell (diameter of the hole ~ 15 mm) with an ultimate pressure of 15–16 GPa in a volume of 0.3 cm^3, which is a

Table. Maximum pressure P (GPa) in the toroid-type cells with various diameters d of the central hole (mm).

d	10	15	25	35	50
P	14	12	10	9	7

record combination of these parameters for single-stage high-pressure cells made of hard alloys [10]. A number of designs employing not only hard alloys but also other high-strength materials have been created. A steel chamber of the top/bottom toroid type with toroidal depressions made in its working surfaces permits producing pressures of up to 7 GPa in volumes of ~ 10 cm^3 and greater [11]. The use of superhard materials makes it possible to reach pressures as high as dozens of GPa in small volumes. Toroid-type (just like lentil-type) cells with the central part made of a synthetic-diamond material of the carbonado type makes it possible to obtain pressures of up to 35 GPa in a volume of 0.1 mm^3 [12]. Pressures of ~ 25 GPa in volumes of 10 mm^3 can be reached with the use of a two-step device on the basis of a toroid-type cell with inserts made of diamond compacts [13]. Apart from the pressure and volume, an important characteristic of a high-pressure cell is the possibility of obtaining maximum information in the course of experiments. In toroid-type cells, the electric leads can easily be introduced into the high-pressure zone and are retained in the working state even after many cycles of pressure rise and relief. The introduction into the toroid-type cell of dozens of wires for measuring physical properties is a routine problem (Fig. 4). The geometry of lentil- and toroid-type cells makes it possible to conduct structural studies by using gaskets which weakly absorb and scatter the incident radiation (e.g., amorphous boron or beryllium for X-ray diffraction studies; Ti–Zr, Ti–Nb, and aluminum alloys or bronzes for neutron-diffraction investigations). The devices that were developed make it possible to study the behavior of solids both in the case of quasi-hydrostatic pressures and under conditions of purely hydrostatic compression (Fig. 5).

Active investigations of the various properties and structure of substances have been performed for more than

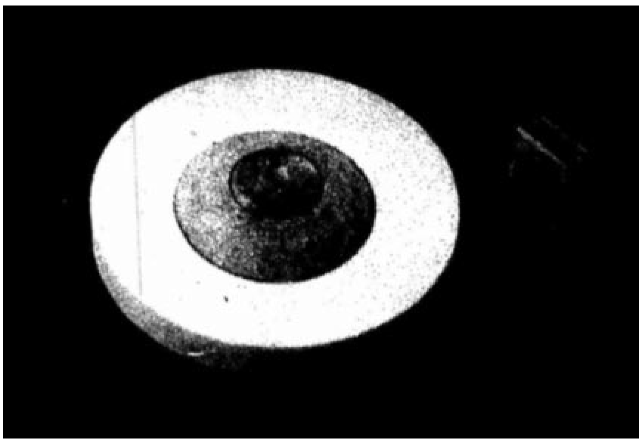

Figure 3. The high-pressure cell of the lentil type with a volume of ~ 200 cm^3.

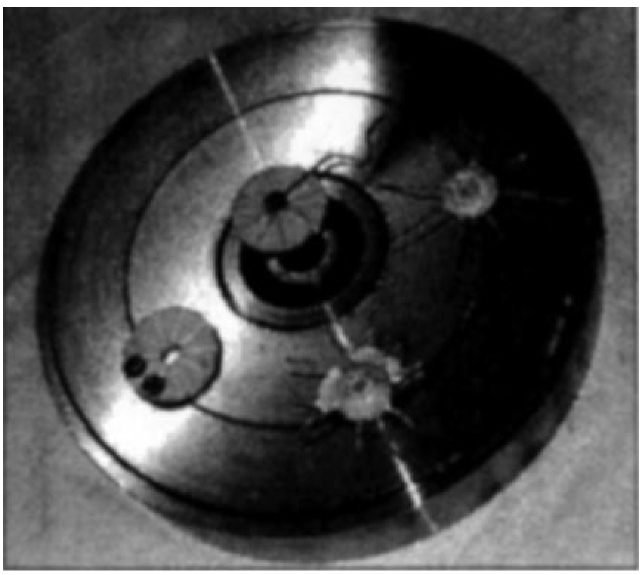

Figure 4. A toroid-type cell with electric leads. Diameter of the central part is 25 mm.

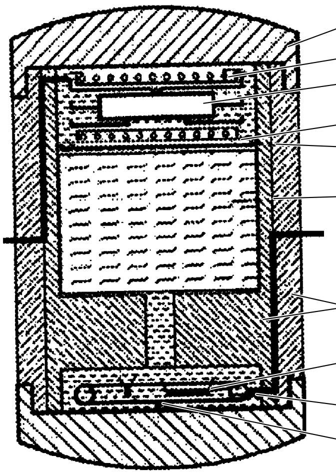

Figure 5. Hydrostatic cell of the toroid-type device.

40 years using these devices in the Soviet Union and Russia in many institutions, e.g., the Institute for High Pressure Physics, Institute of Solid State Physics, Institute of Experimental Mineralogy, Physics Institute of Dagestan Research Center (Russian Academy of Sciences, Russia); Institute of Superhard Materials (Kiev, Ukraine). Because of some specific construction features, the lentil-type cells are suitable predominantly for the synthesis of materials both in the laboratory and in industry, while the majority of electrical measurements and structural studies are performed using cells of the toroid type. Toroid-type cells are also used for high-pressure synthesis of new phases and superhard materials, such as diamonds of the carbonado type and PTNB-type (polycrystalline hard boron nitride) composites.

At the IHPP, various new high-pressure phases in different systems have been synthesized [14–16]. For example, new carbon phases based on fullerites and carbines with unique properties have been prepared [17, 18]; new magnetic and superconductive materials [19], as well as semiconducting and superconducting diamonds [20, 21, 37] have been synthesized; a number of large single crystals of high-pressure phases have been grown, such as diamond, Mg_2Sn, Mg_2Ge, and Mg_2Si phases with an incommensurate structure [22], dense phases of silica (coesite [23] and stishovite [24]), and TiO_2 phases [25] (Fig. 6).

In these four decades, numerous physical studies have been carried out using different methods. The elastic properties of hundreds of substances have been investigated by ultrasonic techniques in a wide range of temperatures and pressures [26, 27]. Systematic studies of the elastic properties of substances in the vicinity of phase transitions under pressure made it possible to explain the mechanisms of some polymorphic and isomorphic transformations. Measurements of the linear dimensions of samples using miniature strain gouges allowed conducting unique studies of relaxation phenomena and transformations in powder systems consisting of ultradisperse particles [28, 29] and in glasses and amorphous solids [30, 31] (see Fig. 4). In the last few years, the tensometric technique of measuring the compressibility of substances has been substantially improved and can now be used for measurements at high temperatures [32]. The use of thermal analysis and differential thermal analysis made it possible to carry out a cycle of studies of thermodynamic anomalies at high pressures, including phase transitions

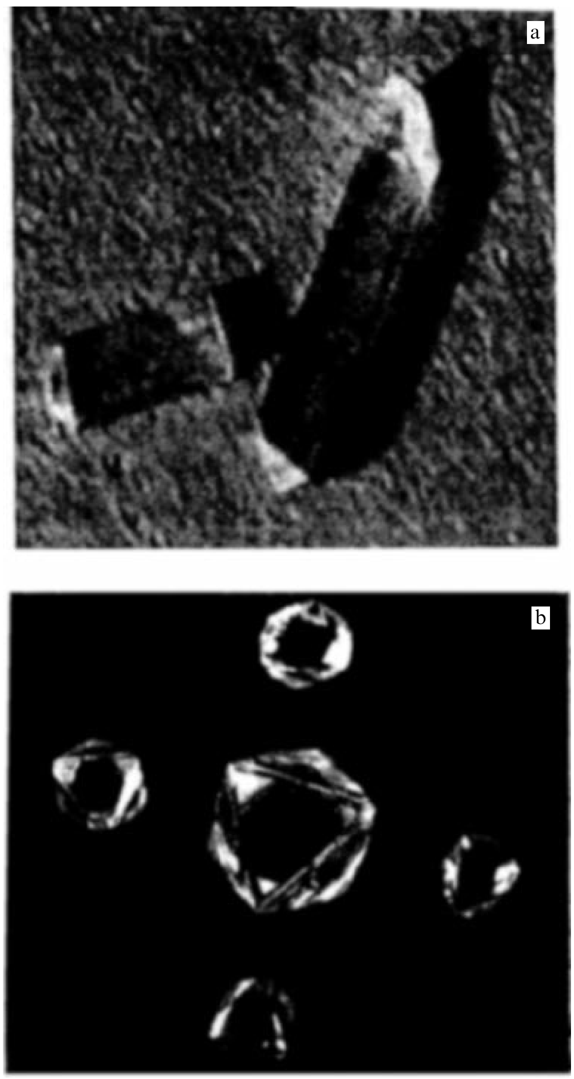

Figure 6. Single crystals of some high-pressure phases synthesized at the IHPP: (a) stishovite, a crystal 3 mm in size; and (b) superconducting diamonds, the central crystal 1.2 mm in size.

between crystalline phases in different classes of materials at high temperatures (to 2000 K) and the melting of substances [33, 34]. The use of thermobaric analysis (TBA) and differential thermal analysis (DTA) together with measurements of electrical resistance made it possible for the first time to study transformations in the melts of elements [35]. Cells with central punches made of Al_2O_3 ceramics supported by rings made of beryllium bronze were used for investigating EPR spectra and magnetic measurements [36]. A wide spectrum of electrophysical investigations under pressure has been performed. Measurements of electrical resistance [40–42] (e.g. by the Van der Pauw method [43]), thermal emf [44, 45], Hall resistance [46, 47], and thermal conductivity [48] have been carried out. Studies of transformations under pressure in semiconductors of different classes [49, 50], including compounds with a variable valence [51, 52], have been performed.

Special modifications of miniature cells of the lentil and toroid types were actively used for X-ray diffraction studies [38, 39]. The structures and phase transformations in dozens of substances at pressures of up to 20 GPa in a wide temperature range have been studied. The miniature cells were widely employed for low-temperature studies, including studying superconductivity under pressure [53, 54]. Active studies of magnetic susceptibility and of magnetic transitions under pressure, as well as of heat capacity (also at low temperatures) were carried out with the use of various types of cells. The miniature cells of the toroid type made of nonmagnetic alloys are at present used for complex studies of quantum phase transitions at ultralow temperatures [55, 56]. Active use of toroid-type cells with anvils made of a hard alloy and diamond composites for neutron research with the use of a neutron source at the Joint Institute for Nuclear Research [57, 58] has begun.

Both at the IHPP and abroad, work on the employment of cells of the lentil and toroid types with the central anvils made of composites on the basis of diamond and cubic boron nitride continue actively, which makes it possible to study the structure and properties of substances in relatively large volumes (several cubic millimeters) in the megabar pressure range.

In the West, high-pressure devices developed in Russia have been in active use in the last 10 – 15 years. The numerous studies carried out in Russia using cells of the toroid and lentil types have demonstrated a number of their advantages over foreign-made devices. In Great Britain, France, the United States, and Japan devices of the toroid type are used to conduct neutron diffraction, X-ray diffraction, and ultrasonic studies. Devices of the toroid and konak (a modification of the lentil type) types are mainly used for the synthesis of new materials.

To conclude, it can be said that cells of the toroid and lentil types give the possibility of conducting structural studies and measurements of various physical properties of substances in the condensed state, and of synthesizing new high-pressure phases in a wide range of pressures and temperatures. They are also very efficient in the industrial production of superhard materials.

References

1. Swenson C A *Physics at High Pressure* (Solid State Phys., Vol. 11) (New York: Academic Press, 1960) [Translated into Russian (Moscow: Mir, 1963)]
2. Bradley C C *High Pressure Methods in Solid State Research* (New York: Plenum Press, 1969) [Translated into Russian (Moscow: Mir, 1972)]
3. Dzhavadov L N *Prib. Tekh. Eksp.* (6) 94 (1996) [*Instrum. Exp. Tech.* **39** 861 (1996)]
4. Khvostantsev L G, Slesarev V N, Brazhkin V V *High Pressure Res.* **24** 371 (2004)
5. Vereshchagin L F, Slesarev V N, Ivanov V E "Prostaya konstruktsiya apparatury dlya sozdaniya davlenii do 100 000 kg/sm^2" ('Simple construction of the apparatus for generation of pressures to 100 000 kg/cm^2'), in *Otchet IFVD AN SSSR* (Report of the Institute for High Pressure Physics, USSR Acad. Sci.) (Troitsk: IFVD, Akad. Nauk SSSR, 1960)
6. Slesarev V N, Candidate's (Phys.-Mat. Sci.) Dissertation (Moscow: Inst. Fiziki Zemli, Akad. Nauk SSSR, 1963)
7. Stishov S M, Popova S V *Geokhimiya* (10) 837 (1961)
8. Vereshchagin L F et al., Inventors Certificate SSSR No. 29199 (1964)
9. Khvostantsev L G, Vereshchagin L F, Novikov A P *High Temp. High. Press.* **9** 637 (1977)
10. Tsiok O B, Khvostantsev L G *Zh. Eks. Teor. Fiz.* **120** 1438 (2001) [*JETP* **93** 1245 (2001)]
11. Khvostantsev L G *High Temp. High. Press.* **16** 165 (1984)
12. Evdokimova V V et al. *High Temp. High. Press.* **8** 705 (1976)
13. Bilyalov Ya R, Kaurov A A, Tsvyashchenko A V *Rev. Sci. Instrum.* **63** 2311 (1992)
14. Popova S V *Phys. Scripta* **T1** 131 (1982)
15. Bendeliani N A *Dokl. Akad. Nauk SSSR* **219** 851 (1974)
16. Dyuzheva T I, Bendeliani N A, Kabalkina S S *J. Less Common Met.* **133** 313 (1987)
17. Brazhkin V V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **76** 805 (2002) [*JETP Lett.* **76** 681 (2002)]
18. Demishev S V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **78** 984 (2003) [*JETP Lett.* **78** 511 (2003)]
19. Tsvyashchenko A V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **78** 864 (1998) [*JETP Lett.* **68** 908 (1998)]
20. Revin O G, Slesarev V N *Sverkhtverd. Mater.* (2) 29 (1982)
21. Ekimov E A et al. *Nature* **428** 542 (2004)
22. Bolotina N B et al. *J. Alloys Comp.* **278** 29 (1998)
23. Dyuzheva T I et al. *Kristallografiya* **43** 554 (1998) [*Crystallogr. Rep.* **43** 511 (1998)]
24. Lityagina L M et al. *J. Cryst. Growth* **222** 627 (2001)
25. Dyuzheva T I, Lityagina L M, Bendeliani N A *J. Alloys Comp.* **377** 17 (2004)
26. Voronov F F *Adv. Space Res.* **1** 147 (1981)
27. Voronov F F *High Temp. High. Press.* **9** 657 (1977)
28. Bredikhin V V et al. *Europhys. Lett.* **18** 111 (1992)
29. Tsiok O B et al. *Phys. Rev. B* **51** 12127 (1995)
30. Tsiok O B, Brazhkin V V, Lyapin A G, Khvostantsev L G *Phys. Rev. Lett.* **80** 999 (1998)
31. Brazhkin V V, Lyapin A G, Tsiok O B *Rev. High Pressure Sci. Technol.* **7** 347 (1998)
32. Yelkin F S, Tsiok O B, Khvostantsev L G *Prib. Tekh. Eksp.* (1) 112 (2003) [*Instrum. Exp. Tech.* **46** 101 (2003)]
33. Bendeliani N A, Vereshchagin L F *Zh. Fiz. Khim.* **6** 1631 (1969)
34. Sidorov V A *Appl. Phys. Lett.* **72** 2174 (1998)
35. Brazhkin V V, Lyapin A G *J. Phys.: Condens. Matter* **15** 6059 (2003)
36. Alaeva T I et al. *Prib. Tekh. Eksp.* (5) 206 (1972)
37. Revin O G, Slesarev V N *Fiz. Tekh. Poluprovodn.* **16** 2219 (1982)
38. Vereshchagin L F, Kabalkina S S *Rentgenostrukturnye Issledovaniya pri Vysokom Davlenii* (X-ray Diffraction Studies at High Pressures) (Moscow: Mir, 1979)
39. Vereshchagin L F, Kabalkina S S *High Temp. High. Press.* **7** 637 (1975)
40. Vereshchagin L F, Atabaeva E Ya, Bendeliani N A *Fiz. Tverd. Tela* **13** 2452 (1971)
41. Khvostantsev L G, Sidorov V A *Phys. Status Solidi A* **82** 389 (1984)
42. Khvostantsev L G, Nikolaev N A *Phys. Status Solidi A* **77**161 (1983)
43. Sidorov V A et al. *Phys. Rev. Lett.* **73** 3262 (1994)
44. Khvostantsev L G, Sidorov V A *Phys. Status Solidi A* **46** 305 (1978)
45. Khvostantsev L G, Nikolaev N A *Phys. Status Solidi A* **51** K57 (1979)
46. Rakhmanina A V et al. *Fiz. Tverd. Tela* **20** 3178 (1978)
47. Mollaev A Yu et al. *Fiz. Tekh. Vys. Davl.* **13** 29 (2003)
48. Vereshchagin L F, Khvostantsev L G, Sidorov V A *High Temp. High. Press.* **9** 628 (1977)
49. Khvostantsev L G, Sidorov V A *Phys. Status Solidi A* **64** 379 (1981)
50. Khvostantsev L G et al. *Phys. Status Solidi A* **89** 301 (1985)
51. Gavrilyuk A G et al. *Fiz. Tverd. Tela* **28** 2135 (1986) [*Sov. Phys. Solid State* **28** 1192 (1986)]
52. Sidorov V A et al. *Fiz. Tverd. Tela* **33** 1271 (1991)
53. Il'ina M A, Itskevich E S *Fiz. Tverd. Tela* **21** 2321 (1979)
54. Il'ina M A, Itskevich E S, Dizhur E M *Zh. Eksp. Teor. Fiz.* **61** 2057 (1971) [*Sov. Phys. JETP* **34** 1263 (1972)]
55. Sidorov V A et al. *Phys. Rev. Lett.* **89** 157004 (2002)
56. Sidorov V A et al. *Phys. Rev. B* **67** 224419 (2003)
57. Glazkov V P et al. *Zh. Eksp. Teor. Fiz.* **121** 1321 (2002) [*JETP* **94** 1134 (2002)]
58. Glazkov V P et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **74** 455 (2001) [*JETP Lett.* **74** 415 (2001)]