High pressure synthesis of solids

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Abstract

The field of high pressure synthesis of solid state compounds is reviewed, for the period between late 1997 through late 1998. The review does not cover syntheses of organic compounds, nor high pressure mineralogy. Emphasis is placed on new solid state compounds discovered during the reviewing period, and on recent findings in on-going areas of high pressure research. The main classes of materials receiving on-going attention are (i) 'super-hard' materials, including compounds based on the diamond structure, advances in the search for C_3N_4, interesting new materials derived from fullerite (C_{60} and C_{70}), and icosahedral borides, and (ii) high T_c oxide superconductors, as well as (iii) other new compounds and classes of compound synthesized for the first time by high pressure techniques. Current research on synthesis of new organometallic compounds prepared at high pressure is also mentioned briefly.   © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The application of high pressure results in a densification of solids, often accompanied by dramatic changes in physical properties, such as electrical conductivity, optical absorption, magnetism, and resistance to shear or compressive stress. Solids synthesized under high pressure conditions tend to have increased first- or second-nearest-neighbor coordination numbers, and often unusual valence states for the constituent atoms. The same solids decompressed to ambient conditions also can exhibit unusual and interesting material properties, due to their metastable 'stretched' state, relative to their equilibrium volume within the high pressure stability field. The pressure variable in synthesis also provides a pathway to unusual metastable compounds, not normally observed in room pressure syntheses, derived from highly energetic precursor materials, by careful design of the pressure–temperature treatment conditions used.

In this review, we focus on recent advances made in the well-known but still relatively unexplored field of high pressure synthesis of inorganic solids, with emphasis on work published during the final part of 1997 through late 1998. This review does not extend to the large body of work devoted to the study of Earth and planetary materials and their phase relations under high pressure–high temperature conditions, which do not strictly correspond to synthesis of new solid state materials. However, there have been several interesting and exciting developments in this field during the past year, some of which are relevant to solid state and materials chemistry [1,2]. We likewise do not include the recent rapid developments in organic synthesis under high pressure conditions, although we note the opportunities afforded by the development of new synthetic pathways at high pressure, including stereoselective syntheses [*3]. In this context, we note the use of 'high' pressure (in the 0.1–1.5 GPa range) to expand the range of reactions involving fullerene molecules, C_{60} [4], including what is presumed to be a cross-linking reaction between C_{60} molecules and polystyrene [*5]. Below, we describe solid state reactions of C_{60} at high pressures and high temperatures, to obtain a new family of 'super-hard' materials. Finally, we neglect those high pressure experiments that belong more truly to the domain of high pressure physics rather than to that of synthetic solid state chemistry, such as the recent report of metallization of the 'quintessential' ionic compound CsI (and its superconductivity) above 108 GPa [*6], the coaxing of elemental sulphur into a superconducting state (with a T_c of 17 K, higher than that recorded for any other element) at 100–157 GPa [*7], or the metallization of hydrogen in the fluid

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state under shock conditions [**8,**9] and its non-metalli-zation under static high pressure conditions in the solid state, to the highest pressures yet attained [10].

2. 'Super-hard' materials

The first target of high pressure laboratory synthesis of a solid state material was diamond, the high pressure phase of carbon, beginning in the late 1800s and culminating with its successful synthesis and commercialization follow-ing the intense activity in the early to mid 1950s . There is still considerable activity in this area. Onodera et al. [11] have reported the catalyzed formation of large (0.3–0.7 mm), transparent, well-formed diamond crystals (with cuboctahedral habit) from phenolic resin precursor in the presence of liquid Co at pressures of 2–4 GPa (20–40 kbar), well below the diamond stability field. The de-composition of the precursor to form free radicals is thought to play an important role in determining the crystallization and growth of the diamond phase outside its thermodynamic stability range. Sung and Tai [12] have summarized the catalytic effect of all of the transition metals in effecting diamond synthesis at high pressure, and have reviewed the mechanisms proposed for stable and metastable diamond crystallization in high pressure–high temperature experiments. Perhaps one of the most interest-ing reports this year was the metastable synthesis of bulk (rather than thin film) nanocrystalline diamond via a metathesis route, in which CCl_4 was reacted with metallic sodium (note the potential danger associated with such experiments!) at 700°C and ambient pressure [**13].

After diamond, a primary target of high pressure syn-thesis groups has been the preparation of other 'super-hard' materials, particularly in the system B–C–N–O. Komatsu et al. [*14] have reported the synthesis of a new hetero-substituted diamond structure with approximate composition $BC_{2.5}N$, prepared at 50 GPa and 3000–10 000°C by explosive shock synthesis from graphitic precursors. Bando et al. [15] have described a fullerene-type compound with a similar composition, synthesized by laser heating in a diamond anvil cell at 5–10 GPa.

A suite of theoretical papers published by M.L. Cohen and co-workers at Berkeley in 1985–1990 stimulated a period of intense interest in the covalent compound C_3N_4, predicted to have a hardness comparable with or exceeding that of diamond [17]. In a recent report, Nguyen et al. [16] have claimed to have synthesized a high pressure phase of this material for the first time. They placed C_{60} particles in a diamond anvil cell with a nitrogen pressure medium, and laser heated the mixture at pressures of 10–60 GPa to temperatures ranging from approximately 100 to 5000 K. Following the synthesis run, the samples were examined in situ at high pressure using synchrotron X-ray powder diffraction. For synthesis pressures and temperatures above 18 GPa and 2000 K, they observed the appearance of a series of weak, sharp diffraction lines, which could be indexed to a cubic phase of C_3N_4 predicted by Teter and Hemley [17]. Nguyen et al. saw no evidence for the β-Si_3N_4 structure considered in the original theoretical work. The bulk modulus measured by Nguyen et al. for the new phase observed in their experiments was much lower than predicted, 249 GPa compared with 496 GPa, and no chemical analysis or spectroscopic information could be obtained. The new C_3N_4 phase was unstable on decom-pression, losing its diffraction lines below 14 GPa. Al-though this result is extremely interesting, at this point, there are no chemical analysis data to indicate that the sample in fact contains both nitrogen and carbon, nor in what ratio, nor how they are bound. The experiments could be repeated using, for example, micro-infrared spectros-copy to study the sample while held at pressure in the diamond cell, to detect or confirm the presence or absence of C–C bonds and terminal or bridging C–N bonds [18].

Nesting et al. [19] have reported preliminary results of similar laser heated diamond cell synthesis experiments, but this time using molecular precursors with fixed C:N ratio, and in which the desired C–N bonds were already present. In particular, they used tetracyanoethylene (TCNE: C_6N4) in laser heating experiments at 2500°C and at 20 and 42 GPa. A transparent orange material containing only carbon and nitrogen (determined by electron energy loss spectroscopy on quenched material) was recovered with a C:N ratio of nearly 3:2 at the higher synthesis pressure. Infrared spectroscopy showed no terminal nitrile (C–N) stretches, indicating that the nitrogen atoms were incorporated in the structure. No diffraction data were reported. In a second experiment, TCNE was mixed with cyanuric triazide (C_3N_{12}) to give a C_3N_4 stoichiometry, and the precursor material was heated at 2500°C and 119 GPa. The resulting product showed a series of weak, broad X-ray diffraction lines (taken in situ at high pressure) that could be indexed to a tetragonal cell with $a = 7.815$, $c = 6.219$. This does not correspond with any of the phases considered in the theoretical study by Teter and Hemley. The decompression behavior of this sample was not described. In their paper, Nesting et al. also describe work in progress using a 'graphitic' form of C_3N_4 containing only C–N bonds (as determined by IR spectroscopy) previously prepared as thin films [18], as a precursor for further high pressure synthesis experiments.

Recent work in our own group has focused on the 'icosahedral boride' class of super-hard materials, with structures related to that of α-rhombohedral boron. Syn-thesis of B_6O_{1-x} at pressures above 3 GPa in a B_2O_3-rich environment yields material close to the nominal com-position (up to $B_6O_{0.96}$) [20]. In the presence of a B_2O_3 flux, these high pressure syntheses yielded large (30–40 μm) near-perfect icosahedral particles in syntheses at 4–5.5 GPa and 1200–1800°C [**21,22]. This unusual mor-phology is the result of multiple twinning of the $R\bar{3}m$ B_6O structure. The icosahedral growth can also be described by

Mackay packing, in which successive shells of icosahedral B_{12} units form around a central icosahedral nucleus. In this work, synthesis of a new material with composition close to B_6N was also reported [22]. The thermodynamic, kinetic and structural factors affecting the nucleation and growth of this unusual morphology are the subject of on-going work.

There has been recent interest in high hardness forms of carbon formed from polymerizing C_{60} and C_{70} at high pressure, and several reports appeared in the proceedings of the last International Conference on High Pressure Science and Technology [2]. Brazhkin et al. [*23] and Lyapin et al. [24] studied the structural nature and properties of materials obtained by treating C_{60} held at 9 and 12.5 GPa at various temperatures. The solid state fullerene became increasingly polymerized (increasing proportion of sp^3 bonds) and X-ray amorphous with increasing synthesis temperature, and the Vickers hardness H (at 1.96 and 5.5 N load) increased to nearly 70 GPa for samples treated at 12.5 GPa and 450°C, compared with diamond [~130 GPa for the (100) faces; ~170 GPa for (111)]. Matsumuro et al. [*25] carried out a similar series of studies, and obtained $H = 104$ GPa for bulk material polymerized at 5.4 GPa and 400°C. Blank et al. [26] carried out pressure-induced polymerization studies for both C_{70} and C_{60} materials, and reported hardnesses (measured by scanning force microscopy) up to 90 ± 10 GPa for polymerized C_{70} and up to 120 ± 10 GPa for polymerized C_{60} materials. These groups studied the polymerization process via X-ray diffraction and vibrational (IR and Raman) spectroscopy, as well as by electron microscopy of the recovered materials. The mechanism for the polymerization/amorphization process is still not clearly understood. Blank et al. [**27] prepared super-hard carbon materials from C_{60} fullerite at up to 13 GPa and up to 2000°C. Samples prepared at the highest pressures had hardnesses that were comparable to or even exceeding that of the diamond indenter used to measure hardness: these authors estimated a hardness equivalent to Vickers hardness of ~300 GPa for samples prepared at 13 GPa. These materials are truly remarkable: they constitute the first solids prepared with a hardness reliably reported to exceed that of diamond. It is expected that increasing attention will be paid to understanding and controlling the high pressure–high temperature polymerization process and characterizing the resulting forms of carbon, to yield a new family of technologically important super-hard materials.

3. Other refractory materials

There has been recent interest in amorphous alloys containing 'borderline' metals such as Si, B and Be in combination with transition metals, which can be quenched directly from the melt. Zhou et al. [28] have found that increasing pressure (to 1.5 GPa) considerably widens the supercooled liquid range of $Ni_{69}Cr_7Fe_{2.5}Si_8B_{13.5}$, permitting the metallic glasses to be formed over a wider range of cooling rates, and permitting maximum densification of the amorphous compacts obtained. In the area of direct synthesis of metal–alloy matrix composites, Liu et al. [29] have reported a similar degree of densification, with formation of highly oriented Al_3Ni whiskers, of composite materials in the Al–Ni system at 1–6 GPa. Suzuki et al. [*30] have discovered an interesting new synthesis route to form thin films of the refractory ceramic TiC on steel substrates by treating successive layers of Ti and polyethylene at room temperature but at high applied pressure (1.45, 10.9 kbar) in the presence of an electric field (37 or 99 MV/m). Bockowski et al. [31] have explored the synthesis and sintering of the important refractory ceramic material AlN from Al metal via combustion synthesis, or self-propagating high-temperature synthesis (SHS) under high N_2 or Ar/N_2 pressures combined with hot-pressing of the recovered AlN powder. This section would be incomplete without a mention of the single crystal growth of GaN, desired as a substrate for homoepitaxial growth of (In, Ga) N blue–green semiconductor LEDs and lasers, which has become the speciality of the high-pressure group in Warsaw [*32].

4. Oxide superconductors

There has been intense activity over the past year in the area of high pressure synthesis of new ceramic superconductors with high values of the superconducting transition temperature, T_c. It is now common practice to use high oxygen pressures (up to several hundred or several thousand atm) during synthesis to control the oxygen content and hence vary T_c of cuprate superconductors, as well as supressing unwanted impurity phases [*33]. Karpinski et al. [34] have recently used high oxygen pressures ($P_{O_2} = 2$ kbar) to synthesize the 'spin-ladder' compound $Sr_{0.73}CuO_2$. This particular low dimensional compound is not superconducting, but is an insulator which shows antiferromagnetic ordering below 135 K. A sharp change in the magnetic properties occurs below 10 K, the temperature at which a superconducting transition occurs in the related compound $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$. Kopnin et al. [35] used high Ar gas pressures to prepare single crystals of $CaCuO_2$, $Sr_{0.53}Ca_{0.47}CuO_2$ and $Ca_{1-x}La_xCuO_2$ (with $x <$ 0.016) for structure refinement and a preliminary study of their magnetic properties and electrical conductivity. These compounds are not found to be superconducting, but they show very interesting magnetic behavior as a function of temperature. The relationship between the magnetism and the superconducting properties in this general class of materials is of considerable current interest [**36].

The Hg-bearing cuprate family of superconductors has the highest values of T_c reliably reported to date, reaching

133 K (for $HgBa_2Ca_2Cu_3O_{8+\delta}$: Hg-1234) at ambient pressure [37]. Morikawa et al. [38] have now demonstrated a high pressure synthesis route of these compounds directly from a mixture of the component oxides. In another recent study, Lokshin et al. [*39] used high pressures (2–4 GPa) to synthesize suites of Hg-1234 and Hg-1223 ($HgBa_2Ca_3Cu_4O_{10+\delta}$) samples. The phase purity of the samples was examined carefully as a function of synthesis temperature and pressure and starting composition. The fraction of Hg-1234 phase in the mixture was maximized for a nominal oxygen content $\delta = 0.2$ in the starting mixture, and there is a strong correlation between the value of T_c and the a cell parameter. The highest values of T_c occur for the Hg-1223 phase with $a = 3.852$ A, for which $T_c = 135$ K was recorded. Further work is needed to precisely determine the oxygen content in the superconducting phases.

The T_c value of Hg-1234 has been found to increase to 164 K when measured in situ at high pressure (30 GPa) [40]. A recent study by Attfield et al. [*33] on a series of A_2CuO_4 compounds (A=La,Nd,Ca,Sr,Ba), demonstrates a peak in T_c (at 39 K) values at a mean A-site cation radius of 1.22. Both of these studies show the great sensitivity of superconducting transition temperatures to lattice strains. Locquet et al. [**41] have used this dependency to double the T_c (from 25 to 49 K) of $La_{1.9}Sr_{0.1}CuO_4$ in a sample prepared in a compressionally strained state by epitaxial growth on a $SrLaAlO_4$ substrate. This could provide a powerful new approach for tuning the superconducting properties of samples prepared in thin film form [*57].

Another family of superconductors that has been receiving recent attention via high pressure synthesis is the class of rare earth-containing superconductors, particularly those containing Pr^{3+}. The parent compound $PrBa_2Cu_3O_2$ (Pr-123) is not superconducting, the reason for which is still not fully understood. Chen and co-workers [42,43] synthesized a series of compounds $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ with R=Nd, Sm, Eu, Gd, Ho and Tm, and found that the superconductivity was suppressed with increasing Pr content. Yao et al. [44] have used high pressure techniques to prepare $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_z$. In highly oxidizing environment (using $KClO_4$ as oxygen source), nearly single phase orthorhombic Ca-doped Pr-123 was formed. This material was found to be superconducting, with $T_c = 52$ K. In reducing environment, a high purity tetragonal material was formed, which had a much higher value of T_c (97 K). This class of materials obviously merits much further study.

High pressure synthesis methods have also been used to explore new families of ceramic superconductors. Iyo et al. [45] have reported synthesis of $(M,C)(Ba,Sr)_2Ca_2Cu_3O_9$ superconductors with M=Al and Ga. The partial substitution of C^{4+} for Al^{3+} or Ga^{3+} was found to enhance T_c. In contrast, Bordet et al. [46] synthesized superconducting mercury cuprates $(Hg_{1-x}M_x)Ba_2Ca_{n-1}Cu_nO_{2+2n+\delta}$ with

partial replacement of mercury with C or S (=M). Depending on the synthesis pressure in the system with carbonate precursors, recovered samples consisted either of polyphase mercury barium copper oxides and carbonates, or nearly single phase $HgBa_4Cu_2CO_3O_y$. This material, containing carbonate groups in the Hg layer, was not found to be superconducting. Matseev et al. [47] and Kawashima et al. [48] have used the high pressure synthesis route to prepare a new family of superconducting copper oxycarbonates $(CCa_2Ca_{n-1}Cu_nO_{2+3n+\delta})$ and oxyborates $(BSr_2Ca_{n-1}Cu_nO_{2+3n})$. These compounds were prepared at 5–6 GPa pressure, and were found to have T_c values reaching 43 K (for $n=1$) for the oxycarbonate series and 110 K for the oxyborate with $n=4$. The use of high pressure in these syntheses permitted substitution of the small atoms B and C in the 'blocking layer', normally occupied by large metal cations. It is apparent from these intriguing, but obviously preliminary and often conflicting observations, that the high pressure route offers additional control over experimental synthesis parameters to expand the search for high T_c materials to a wide range of new chemical systems: however, work in this area is only just beginning.

5. Other solid state compounds

The field of experimental mineralogy continues to yield interesting new solid state compounds. Wunder and Marler [49] have reported the high pressure synthesis (2 GPa, 650°C) of a new aluminogermanate topaz-structured material, with composition $Al_2GeO_4(OH)_2$. Park and Parise [50] have reported the synthesis of a new chromite perovskite ($ScCrO_3$) at 4.5 GPa and 1200°C, and determined its crystal structure. This family of compounds is receiving renewed attention because of its interesting magnetic ordering behavior [*51]. Troyanchuk et al. [52] have used high pressure to prepare a series of solid solutions $La_{1-x}Pb_xMnO_3$ as well as the compound $La_{0.56}Pb_{0.44}MnO_{2.56}F_{0.44}$, containing Mn ions in mixed valence (Mn^{3+}–Mn^{4+}) states. These materials with the perovskite structure show a 'collosal magnetoresistance' (CMR) effect. Kanke [53] has reported the first synthesis of the mixed valence (V^{3+}–V^{4+}) oxides KV_6O_{11} and BaV_6O_{11}, by preparation from the oxides at 5.5 GPa and 1200–2000°C. Park et al. [54] have recently used high pressure synthesis (14 GPa, 1000°C) in a multi-anvil apparatus to obtain two new perovskite compounds containing monovalent silver, $Ca_2NdAgTi_4O_{12}$ and $NdAgTi_2O_6$, with an unusual layered ordering of the Nd^{3+} and Ag^+ A-site cations. The same group has now reported a very interesting use of the high pressure variable to synthesize a new high dielectric perovskite-structured material, $(Bi_{1/2}Ag_{1/2})TiO_3$, also with Ag^+ on the A site [**55]. This orthorhombically distorted perovskite struc-

ture has a static (100 kHz) dielectric constant of 350, rising to $\epsilon \sim 1400$ at 580 K, in the vicinity of an orthorhombic–tetragonal transition. The principle used by these workers to identify candidates for high dielectric materials prepared at high pressure, based on general correlations expected between the dielectric properties and bulk density, should prove extremely powerful in future investigations.

Over the past decade or so, considerable attention has been paid to the field of 'pressure-induced amorphization', in which a glassy material is formed by metastable compression of a crystalline solid at a temperature low enough to preclude crystal–crystal phase transitions on the experimental timescale. This method, of essentially physical interest in most cases, can be employed to obtain amorphous materials in systems which are difficult glass formers. This is the case for ZrW_2O_8, which was not known previously as a bulk glass by melt quenching, which has been rendered amorphous by high pressure treatment at room temperature [**56]. This crystalline material is remarkable in that it contracts upon heating, due to thermal excitation of deformational modes and bridging oxygen vibrations of and between the ZrO_6 and WO_4 units. This general class of compounds with 'negative compressibilities' is currently receiving considerable attention within the materials science community [*57].

At or near ambient pressure, the alkali metals do not react with any of the transition metals except for gold. However, Parker et al. have conducted a series of experiments over the past few years demonstrating that whole series of new compounds are formed in the K–Ag, K–Ni and K–Pd systems [*58]. Hasegawa et al. [*59] have recently reported the synthesis of a new phase KAg_2 with the C14 Laves structure following compression of a stoichiometric mixture of the elements to 7 GPa in a diamond anvil cell. Although the product formed at ambient temperature, laser heating was used to improve the crystallinity. This is a rich area for further investigation, as formation of these compounds implies a change in the alkali metal electronic structure via pressure-induced mixing of the 4s- and 3d-states.

Compared to other families of materials, there have been relatively few investigations of the solid state chemistry of chalcogenide compounds at high pressure in general, and this reporting period is no exception. Poulsen [60] has reported the high pressure synthesis and Rietveld structure analysis of a solid solution series $((Ba,K)VS_3)$. This family of compounds based on the $BaNiO_3$ structure is interesting because of their low-dimensional magnetic and electronic properties, and they deserve much more attention in the future. The whole family of chalcogenides, with their structures linked into oligomers, chains, sheets, and networks by chalcogen–chalcogen bonding correlated with variable dimensionality of their electronic, optical and magnetic properties, provide a rich area for future explorations in high pressure synthesis studies.

Like the chalcogenides, the pnictides (containing P, As, Sb) and tetrelides (with Si, Ge, Sn) have received much less attention in high pressure synthetic studies than the first-row oxides, nitrides and carbides, and this area constitutes a rich field for future investigations. Shirotani et al. [61] have used high pressures (~4 Gpa) to prepare the new superconducting ($T_c \sim 10$ K) materials $ZrNi_4P_2$ and Mru_4P_2, with M = Zr and Hf. Evers et al. [**62] have used a high pressure route to synthesize for the new Zintl phase LiSi, the missing first member of the alkali metal monosilicides. In a highly entertaining article, they describe the strategy devised to synthesize this compound, and discuss the thermodynamic considerations that prevented its obtention in prior studies at ambient conditions. Unlike the other alkali metal silicides which contain isolated tetrahedral Si_4^{4-} anions, LiSi contains a three-dimensional, three-connected net of silicon atoms with large cavities occupied by the Li^+ cations.

6. Organometallic and molecular compounds

The high pressure variable, usually in the 1–10 kbar (0.1–1 GPa) range, has been used previously in the synthesis and study of transition metal complexes. In a recent study, Boudin and Lii [*63] have used hydrothermal synthesis at pressures of several kbars to synthesize single crystals of $NH_4Fe_2(PO_4)_2$, the first example of a mixed-valence ammonium iron phosphate. The utilization of high pressure fluids in the supercritical state is yielding new compounds, particularly those with labile ligands. Ferrence et al. [64] have employed a high pressure Parr reactor (~1000–1300 p.s.i.) to prepare a new series of Ru–Ru bridged complexes. Lee et al. [**65] have used supercritical CO_2 as a solvent to prepare a new series of cyclopentadienyl compounds with labile C_2H_4 and H_2 as ligands. This rapidly developing field is certain to yield a wide range of new compounds which were difficult to stabilize using previously existing methods. As the range of new organic syntheses at high pressures is opened up [*3], we can expect a further infusion of new preparative strategies in organometallic chemistry.

Finally, Somayazulu et al. [*66] have reported the 'synthesis' of a new family of 'compounds' formed between methane and hydrogen, held together in a diamond anvil cell at pressures up to 36 GPa. These new phases have compositions $CH_4(H_2)_4$, $(CH_4)_2H_2$, and a phase of unknown stoichiometry $(CH_4)_m(H_2)_n$. They are not 'normal' chemical compounds in that the bonding between the closed shell molecules are very weak; however, their existence is not determined by simple packing of the constituent molecules either. Work is in progress to further characterize these phases which only exist at high pressure, and to understand the bonding in them.

7. Conclusions

The past year has seen significant advances in the high pressure synthesis of oxide superconductors and related ceramic materials with interesting and potentially useful electronic properties. The use of the high pressure synthesis variable significantly expands the range of compositions that can be made, and can be used to achieve even higher values of T_c. The range of lattice strains induced in high T_c compounds and also high dielectric materials can also be achieved by control of the lattice mismatch during epitaxial growth on suitable substrates, and this too can be used to tune the electronic properties. A new family of carbon-based 'super-hard' materials is obtained by pressurizing C_{60} and C_{70}: work is just beginning to characterize these interesting new materials, and to control the polymerization process. There remain fleeting glimpses of what may be super-hard high pressure phases of carbon nitride C_3N_4, but no reliable high pressure syntheses or characterization has been done. The rhombohedral boron suboxide (B_6O_{1-x}) yields an interesting icosahedral particle morphology at pressures in the 4.5–7 GPa range, due to multiple twinning or Mackay growth. New silicides and phosphides are formed at high pressure: the field for compounds such as these is only just beginning. Finally, significant opportunities exist for synthesis of new organometallic compounds at more moderate pressures, in the supercritical solvent regime.

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References

Papers of particular interest, published within the annual period of review, have been highlighted as:
* of special interest;
** of outstanding interest

[1] Manghnani MH, Yagi T, editors, Properties of earth and planetary materials, American Geophysical Union, Washington, DC, 1998.
[2] Nakahara M, editor, Proceedings of International Conference—AIRAPT-16 and HPCJ-38—on High Pressure Science and Technology, Japan Society of High Pressure Science and Technology, 1998.
[*3] Ciobanu M. Recent advances in organic synthesis under high pressure. Liebigs Ann Org Bioorg Chem 1997;623–35.
[4] Mori S, Karita T, Sugita N, Wan TSM. High pressure synthesis of cycloadduct of fullerene C_{60} with 2H-pyran-2-one. Synth Comm 1997;29:1475–82.

[*5] Kojima Y, Matsuoka T, Takahashi H, Kurachi T. High-pressure synthesis of C_{60}-containing polystyrene. J Mat Sci Lett 1997;16:999–1001.
[*6] Eremets MI, Shimizu K, Kobayashi TC, Amaya K. Metallic CsI at pressures of up to 220 GigaPascals. Science 1998;281:1333–5.
[7] Struzhkin VV, Hemley RJ, Mao H-K, Timofeev YA. Superconductivity at 10–17 K in compressed sulphur. Nature 1997;390:382–3.
[**8] Nellis WJ, Weir ST, Mitchell AC. Electrical conductivity and metallization of fluid hydrogen in the pressure range 90–180 GPa (0.9–1.8 Mbar). Rev High Pressure Sci Technol 1998;7:870–2.
[**9] Collins GW, Da Silva LB, Celliers P, Gold DM, Foord ME, Wallace RJ, Ng A, Weber SV, Budil KS, Cauble R. Measurements of the equation of state of deuterium at the fluid insulator–metal transition. Science 1998;281:1178–81.
[10] Narayana C, Luo H, Orloff J, Ruoff AL. Solid hydrogen at 342 GPa: no evidence for an alkali metal. Nature 1998;393:46–9.
[11] Onodera A, Terashima K, Urushihara T, Sumiya H, Satoh S. High-pressure synthesis of diamond from phenolic resin. J Mat Sci 1997;32:4309–18.
[12] Sung C-M, Tai M-F. Reactivities of transition metals with carbon: implications to the mechanism of diamond synthesis under high pressure. Int J Refract Metals Hard Mater 1997;15:237–56.
[**13] Li Y, Quian Y, Liao H, Ding Y, Yang L, Xu C, Li F, Zhou G. A reduction–pyrolysis–catalysis synthesis of diamond. Science 1998;281:246–7.
[*14] Komatsu T, Kakudate Y, Fujiwara S. Explosive shock synthesis and characterization of a B–C–N heterodiamond. Rev High Pressure Sci Technol 1998;7:983–5.
[15] Bando Y, Golberg D, Stephan O, Tamiya T. High resolution analytical electron microscopy of BN nanotube and small nested–fullerenes of BN and BC_2N. In: Proceedings of the Fifth NIRIM International Symposium on Advanced Materials (ISAM '98), National Institute for Research in Inorganic Materials, Tsukuba, 1998:145–8.
[16] Nguyen JH, Caldwell WA, Benedetti LR, Kruger MB, Jeanloz R. High pressure–high temperature synthesis of low-compressibility cubic C_3N_4. Mat Res Symp 1998;499:303–8.
[17] Teter DM, Hemley RJ. Low-compressibility carbon nitrides. Science 1996;271:53–5.
[18] Kouvetakis J, Bandari A, Todd M, Wilkens B, Cave N. Novel synthetic routes to carbon–nitrogen films. Chem Mater 1994;6:811–4.
[19] Nesting DC, Kouvetakis J, Badding JV. The use of novel molecular precursors for the high pressure synthesis of metastable materials. In: Proceedings of the Fifth NIRIM International Symposium on Advanced Materials (ISAM '98), National Institute for Research in Inorganic Materials, Tsukuba, 1998:1–4.
[20] Hubert H, Garvie LAJ, Buseck PR, Petuskey WT, McMillan PF. High-pressure, high-temperature syntheses in the B–C–N–O system: Part I: Preparation and characterization. J Solid State Chem 1997;133:356–64.
[**21] Hubert H, Devouard B, Garvie LAJ, O'Keeffe M, Buseck PR, Petuskey WT, McMillan PF. Icosahedral packing of B_{12} icosahedra in boron suboxide (B_6O). Nature 1998;391:376–8.
[22] Hubert H, Garvie LAJ, Devouard B, Buseck PR, Petuskey WT, McMillan PF. High-pressure, high-temperature synthesis of boron suboxide (B_6O). Chem Mat 1998;10:1530–7.
[*23] Brazhkin VV, Lyapin AG, Lyapin SG, Popova SV, Voloshin RN, Antonov YuA. Structural transformations in fullerite C_{60} under high-pressure ($P = 12.5$ GPa) and high-temperature conditions. Rev High Pressure Sci Technol 1998;7:817–9.
[24] Lyapin AG, Brazhkin VV, Lyapin SG, Popova SV. Three-dimensional polymerization of fullerite C_{60} under high pressure. Rev High Pressure Sci Technol 1998;7:811–3.
[*25] Matsumoro A, Takada Y, Takashu Y, Kondo I, Senoo M. Mechanical properties of C_{60} bulk materials synthesized at high pressure. Rev High Pressure Sci Technol 1998;7:823–5.

[26] Blank VD, Buga SG, Serebryanaya NR, Dubitsky GA, Sulyanov SN. Phase transformations of C_{70} fullerite under high pressure of 6.5–12.5 GPa and temperature 300–1720 K: comparison with C_{60}. Rev High Pressure Sci Technol 1998;7:814–6.

[**27] Blank VD, Buga SG, Serebryanaya NR, Dubitsky GA, Popov MYu, Prokhorov VM, Lvova NA, Sulyanov SN. High pressure synthesis, structure, physical and mechanical properties of C_{60} fullerite superhard and ultrahard phases. Rev High Pressure Sci Technol 1998;7:972–4.

[28] Zhou F, Zhang XH, Lu K. Synthesis of bulk amorphous ally by consolidation of the melt-spun amorphous ribbons under high pressure. J Mat Res 1998;13:784–8.

[29] Liu H, Wang A, Wang L, Ding B, Hu Z. In situ synthesis of Al_3Ni_w/Al composites under high pressure. J Mat Sci Lett 1997;16:134–6.

[*30] Suzuki K, Nihei T, Ikeda S, Matsuura M, Matsumoto K. New synthesis method of TiC film by applying high pressure and electric field. Jpn J Appl Phys 1997;36:1223–7.

[31] Bockowski M, Witek A, Krukowski S, Wroblwski M, Porowski S, Marin-Ayral RM, Tedenac JC. Combustion synthesis of aluminum nitride under high pressure of nitrogen and nitrogen–argon mixtures. J Mat Synthesis Proc 1997;5:449–58.

[**32] Lucznik B, Bockowski M, Wrobleski M, Grzegory I, Krukowski S, Nowak G, Leszczynski M, Teisseyre G, Pakula K, Baranowski JM, Suski T, Porowski S. GaN single crystals grown by high pressure solution method. Rev High Pressure Sci Technol 1998;7:760–2.

[*33] Attfield JP, Kharlanov AL, McAllister JA. Cation effects in doped La_2CuO_4 superconductors. Nature 1998;394:157–9.

[34] Karpinski J, Schwer H, Meijer GI, Conder K, Kopnin EM, Rossel C. High-oxygen-pressure synthesis, structure and properties of the infinite-chain compound $Sr_{0.73}CuO_2$. Physica C 1997;274:99–106.

[35] Kopnin EM, Schwer H, Jun J, Meijer GI, Molinski R, Conder K, Karpinski J. $Ca_{1-x}R_xCuO_2$ (R = Sr, La) single crystals with infinite-layer structure: high Ar gas pressure synthesis and properties. Physica C 1997;282–287:483–4.

[**36] Mayaffre H, Auban-Senzier P, Nardone M, JÄrome D, Pilblanc D, Bourbonnais C, Ammerahl U, Dhalenne G, Revecolevschi A. Absence of a spin gap in the superconducting ladder compound $Sr_2Ca_{12}Cu_{24}O_{41}$. Science 1998;279:345–8.

[37] Schilling A, Cantoni M, Guo JD, Ott HR. Superconductivity above 130 K in the Hg–Ba–Ca–Cu–O system. Nature 1993;362:56–8.

[38] Moriwaki Y, Tatsuki T, Tokiwa-Yamamoto A, Tamura T, Adachi S, Tanabe K. High pressure synthesis of $HgBa_2Ca_2Cu_3O_y$ without a precursor. J Mat Sci Lett 1997;16:115–6.

[*39] Lokshin KA, Kuzemskaya IG, Kulikova LF, Antipov EV, Itskevich ES. High pressure synthesis of Hg-1234 and strongly-overdoped Hg-1223 phases. Physica C 1997;279:11–7.

[40] Gao L et al. Superconductivity up to 164 K in $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ (m = 1,2 and 3) under quasihydrostatic pressures. Phys Rev B 1994;50:4260–3.

[**41] Locquet J-P, Perret J, Fompeyrine J, Machler E, Seo JW, Van Tendeloo G. Doubling the critical temperature of $La_{1.9}Sr_{0.1}CuO_4$ using epitaxial strain. Nature 1998;394:453–6.

[42] Chen T-M, Kao FS. The high-pressure synthesis and characterization of some praseodymium-substituted rare-earth based $R_2Ba_4Cu_7O_{14+\delta}$ (R = Nd, Eu, Tm). J Solid State Chem 1997;132:73–7.

[43] Chen T-M, Lai Y-L, Kao FS. The high-pressure synthesis and characterization of some praseodymium-substituted rare-earth based $R_2Ba_4Cu_7O_{14+\delta}$ (R = Nd, Sm, Eu, Gd, Ho, Tm). Physica C 1997;282–287:789–90.

[44] Yao YS, Xiong YF, Jin D, Li JW, Wu F, Luo JL, Zhao ZX. The high-pressure synthesis and superconductivity of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_z$. Physica C 1997;282–287:49–52.

[45] Iyo A, Saya T, Tokiwa K, Tanaka Y, Terada N, Tokumoto M, Ihara H. High-pressure synthesis of $(M,C)(Ba,Sr)_2Ca_2Cu_3O_9$ (M = Al and Ga). Physica C 1997;282–287:509–10.

[46] Bordet P, Loureiro S, LeFloch S, Capponi JJ, Chaillout C, Chevanas J, Tholence JL, Antipov EV, Radaelli PG, Marezio M. High pressure synthesis and structure of the superconducting mercury cuprates $(Hg_{1-x}M_x)Ba_2Ca_{n-1}Cu_nO_{2+2n+\delta}$ with M = C, S. Physica C 1997;282–287:65–8.

[47] Matseev AT, Matsui Y, Yamaoka S, Takayama-Muromachi E. High-pressure synthesis of a new oxycarbonate superconductor $Cca_3Cu_2O_{7+\delta}$. Physica C 1997;288:185–9.

[48] Kawashima T, Matsui Y, Takayama-Muromachi E. High pressure synthesis and superconducting properties of oxyborate superconductors, $BSr_2Ca_{n-1}Cu_nO_{2+3n}$ (n = 3~6). In: Proceedings of the Fifth International Symposium on Advanced Materials (ISAM '98), National Institute for Research in Inorganic Materials, Tsukuba, 1998:229–32.

[49] Wunder B, Marler B. Ge-analogues of aluminium silicates: high-pressure synthesis and properties of orthorhombic $Al_2GeO_4(OH)_2$. Eur J Mineral 1997;9:1147–58.

[50] Park J-H, Parise JB. High pressure synthesis of a new chromite $ScCrO_3$. Mat Res Bull 1997;32:1617–24.

[*51] Ueda K, Tabata H, Kawai T. Ferromagnetism in $LaFeO_3$–$LaCrO_3$ superlattices. Science 1998;280:1064–6.

[52] Troyanchuk IO, Khalyavin DD, Szymczak K. High pressure synthesis and study of magnetic and transport properties of Pb-substituted manganites with perovskite structure. Mat Res Bull 1997;32:1637–42.

[53] Kanke Y. High pressure synthesis of mixed valence vanadium oxides KV_6O_{11} and BaV_6O_{11}. In: Proceedings of the Fifth International Symposium on Advanced Materials (ISAM '98), National Institute for Research in Inorganic Materials, Tsukuba, 1998:221–4.

[54] Park J-H, Woodward PM, Parise JB. Predictive modelling and high pressure–high temperature synthesis of perovskites containing monovalent silver. Chem Mater 1998;10:3092–100.

[**55] Park J-H, Woodward PM, Parise JB, Reeder RJ, Lubomirsky L, Stafsudd O. Synthesis, structure and dielectric properties of $(Bi_{1/2}Ag_{1/2})TiO_3$. J Solid State Chem, accepted for publication.

[**56] Perottoni CA, da Jornada JAH. Pressure-induced amorphization and negative thermal expansion in ZrW_2O_8. Science 1998;280:886–9.

[*57] Baughmann RH, Strafstrom S, Cui C, Dantas SO. Materials with negative compressibilities in one or more dimensions. Science 1998;279:1522–4.

[*58] Parker LJ, Hasegawa M, Atou T, Badding JV. High pressure synthesis of alkali metal–transition metal compounds. Eur J Solid State Inorg Chem 1997;34:693–704.

[*59] Hasegawa M, Atou T, Badding JV. High-pressure synthesis of an alkali metal–transition metal Laves phase: KAg_2. J Solid State Chem 1997;130:311–5.

[60] Poulsen NJ. High pressure synthesis, structure solution and Rietveld refinement of polycrystalline $(Ba,K)VS_3$ from X-ray powder diffraction data. Mat Res Bull 1997;32:1673–81.

[61] Shirotani I, Iwasaki G, Kaneko I, Todo S, Yagi T. Electrical conductivity and superconductivity of $ZrNi_4P_2$ and MRu_4P_2 (M = Zr and Hf) prepared under high pressure. Rev High Pressure Sci Technol 1998;7:697–9.

[**62] Evers J, Oehlinger G, Sextl G. LiSi, a unique Zintl phase: although stable, it long evaded synthesis. Eur J Solid State Inorg Chem 1997;34:773–84.

[*63] Boudin S, Lii K-H. Ammonium iron (II,III) phosphate: hydrothermal synthesis and characterization of $NH_4Fe_2(PO_4)_2$. Inorg Chem 1998;37:799–803.

[64] Ferrence GM, Fanwick PE, Kubiak CP, Haines RJ. High-pressure synthesis of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_4$, $[Ru_2(\mu\text{-dppm})$ (μ-

dmpm)(μ-CO)(CO)$_4$], and [Ru$_2$(dcypm)$_2$ (CO)$_3$] from Ru$_3$(CO)$_{12}$ and the diphosphines: R$_2$PCH$_2$PR$_2$; R$=$CH$_3$ (dmpm), C$_6$H$_5$ (dppm) and C$_6$H$_{11}$ (dcypm). Crystal and molecular structures of [Ru$_2$(μ-dppm)(μ-dmpm)(μ-CO)(CO)$_4$], and [Ru$_2$(dcypm)$_2$ (CO)$_3$]. Polyhedron 1997;16:1453–9.

[**65] Lee PD, King JL, Seebald S, Poliakoff M. Thermal exchange reactions of η^5-C$_5$R$_5$)Mn(CO)$_2$(^{w}L) compounds (^{w}L$=$weakly-bound ligand) in supercritical fluid solution and the isolation of η^5-C$_5$R$_5$)Mn(CO)$_2$ η^2-H$_2$) using high-pressure flow and semiflow reactors. Organometallics 1998;17:524–33.

[*66] Somayazulu M, Hemley RJ, Goncharov AF, Mao H-K, Finger LW. High-pressure compounds in the methane–hydrogen system: X-ray, infrared and Raman studies on CH$_4$(H$_2$)$_2$. Eur J Solid State Inorg Chem 1997;34:705–13.