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Novel superhard B–C–O phases predicted from first principles†

Shengnan Wang,*[a] Artem R. Oganov,*[abce] Guangrui Qian,[a] Qiang Zhu,[a] Huafeng Dong,[a] Xiao Dong[d] and M. Mahdi Davari Esfahani[a]

We explored the B–C–O system at pressures in the range 0–50 GPa by *ab initio* variable-composition evolutionary simulations in the hope of discovering new stable superhard materials. A new tetragonal thermodynamically stable phase B_4CO_4, space group $I\bar{4}$, and two low-enthalpy metastable compounds ($B_6C_2O_5$, B_2CO_2) have been discovered. Computed phonons and elastic constants show that these structures are dynamically and mechanically stable both at high pressure and zero pressure. B_4CO_4 is thermodynamically stable at pressures above 23 GPa, but should remain metastable under ambient conditions. Its computed hardness is about 38–41 GPa, which suggests that B_4CO_4 is potentially superhard.

I Introduction

Superhard materials (*i.e.* materials with Vickers hardness exceeding 40 GPa) have always fascinated humans due to their wide range of applications in fundamental scientific research and broad industrial sectors.[1–4] Most hard materials are formed by short and strong covalent bonds, *e.g.* diamond, boron,[5–7] boron nitride,[8–10] carbon nitride,[11] and boron suboxide (B_6O).[12,13] It is known that diamond is the hardest material with a measured polycrystalline hardness at ∼90 GPa. However, it is brittle, becomes unstable in the presence of oxygen at temperatures above 1000 K, and easily reacts with iron by forming iron carbides. Currently, cubic BN with a hardness of 50–60 GPa is widely used to cut ferrous metals.[14] The search for new superhard materials never stopped, and recently, many investigations focused on compounds of light elements with strong covalent bonds in binary B–N, C–N and ternary B–C–N and B–C–O systems.

In experiments, materials such as $B_6C_{1.1}O_{0.33}$ and $B_6C_{1.28}O_{0.31}$ were first produced by reacting mixtures of B, C, and B_2O_3 in the pressure range from 5 to 7.5 GPa and at 1900 K.[15] In addition, $B(CO)_{0.155}$ was obtained by a reaction between B_4C and B_2O_3 at 5.5 GPa and 1400 K.[16] However, unlike B–C–N compounds,[17] the B–C–O compounds with a simple stoichiometric ratio have not yet been synthesized. Recent theoretical work indicated that diamond-like B_2CO is a potentially superhard material with a predicted Vickers hardness exceeding 50 GPa.[18] However, thermodynamic stability of this compound has not been analyzed, and other possible stoichiometries were not explored. In this paper, we systematically study the high-pressure behavior of the B–C–O system at pressures from 0 to 50 GPa using the *ab initio* evolutionary algorithm USPEX.[19–22] We found one stable ternary compound, B_4CO_4. The stability of B_4CO_4 has been confirmed and several metastable phases also have been discovered at low pressure. It turns out that previously proposed B_2CO[18] is unstable.

II Methodology

Using the evolutionary algorithm USPEX,[19–22] we carried out structure and stoichiometry predictions to find all possible stable phases in the B–C–O system. Predictions were done using the variable-composition method at 0, 10, 25 and 50 GPa pressures. This method has been successfully applied to a large number of different systems and resulted in a number of important at high pressures (*e.g.* ref. 23–25). Given the experimental processes to produce B–C–O compounds and the nature of complex bonding types in the ternary B–C–O system, we mainly pursued two strategies to make the stoichiometry and structure predictions. First, the evolutionary prediction was been done in pseudo-binary systems such as B_4C–B_2O_3, B_4C–CO_2 and B_6O–CO_2. Second, we performed a full search in the ternary B–C–O system, allowing up to 40 atoms per unit cell. Stable compounds and the phase diagram (Fig. 1) were determined

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[a] *Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, NY 11794-2100, USA. E-mail: shengnan.wang@stonybrook.edu*
[b] *Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 3 Nobel St., Moscow 143026, Russia. E-mail: artem.oganov@stonybrook.edu*
[c] *Department of Problems of Physics and Energetics, Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny City, Moscow Region 141700, Russia*
[d] *Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China*
[e] *International Center for Materials Design, Northwestern Polytechnical University, Xi'an, 710072, China*

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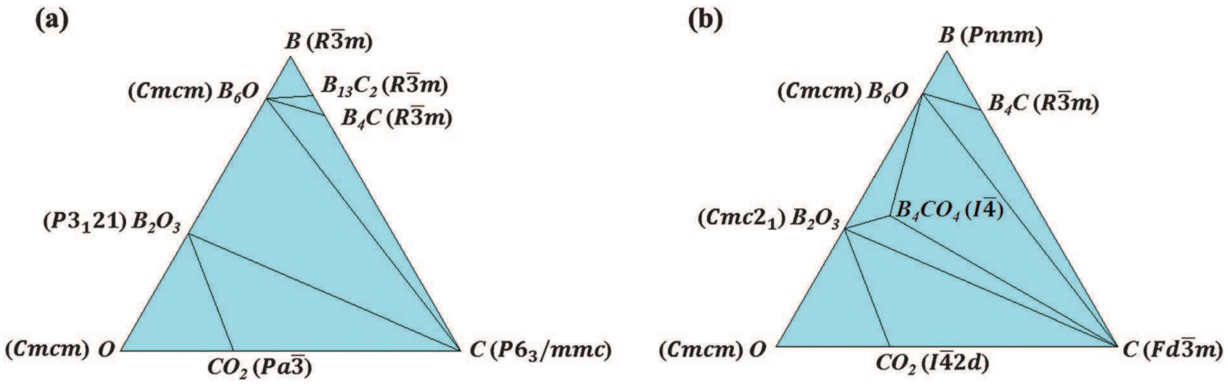

Fig. 1 Phase diagrams of the B–C–O system at (a) 0 GPa, (b) 25 GPa and zero temperature.

using the convex hull construction: a compound is thermodynamically stable when its free energy (at $T = 0$ K, enthalpy) of formation from the elements and from any other compound is negative. For completeness we also included structures from the Inorganic Crystal Structure Database (ICSD)[26,27] in this calculation.

During evolutionary searches, all structures were relaxed; structure relaxations were done within density functional theory (DFT)[28] in the framework of all-electron projector-augmented wave (PAW)[29] method as implemented in the VASP code.[30,31] The exchange–correlation potential was approximated by the Perdew–Burke–Ernzerhof functional at the generalized approximation (GGA)[32] level of theory. The plane-wave kinetic energy cutoff of 550 eV and Γ-centered k-point meshes with the reciprocal-space resolution of $2\pi \times 0.04$ Å^{-1} were used. Having identified the most promising compounds and their structures, we re-relaxed them with more precise calculations using a plane-wave cutoff of 600 eV at pressures from 1 atm to 50 GPa until net forces on atoms were below 1 meV Å^{-1}, which gave us enthalpies converged to better than 1 meV per atom. Phonon dispersion curves were calculated using the finite-displacement approach as implemented in the PHONOPY code.[33] To perform phonon calculations, all the structures were fully relaxed with a cutoff of 600 eV and relaxation proceeded until all force components became by absolute value less than 0.01 meV Å^{-1}. We constructed $3 \times 3 \times 3$ supercells, and displaced atoms by 0.01 Å to get the forces, which were then used to construct the force constants matrix. In these calculations, we employed uniform $3 \times 3 \times 3$ k-points grids for Brillouin zone integration and the energy convergence threshold was set as 1×10^{-8} eV per cell. The elastic constants were calculated from strain–stress relations, as implemented in VASP,[34] and the magnitude of the deformation was 0.015 Å.

III Results and discussions

Notably, a novel B–C–O compound – B_4CO_4 was found to be stable above 23 GPa (Fig. 1). B_4CO_4 belongs to the tetragonal space group $I\bar{4}$ ($a = 5.740$ Å, $c = 3.717$ Å at zero pressure), in which B, C, and O atoms occupy the Wyckoff positions 8g (0.6953, 0.8972, 0.0000), 2d (0.0000, 0.5000, 0.7500) and 8g (0.8883, 0.7831, 0.2100), respectively. As shown in Fig. 2, the main feature of B_4CO_4 is the presence of B–C and B–O bonds and tetrahedrally coordinated B and C atoms. The average B–C and B–O bond lengths are about 1.570 Å and 1.539 Å at ambient pressure. Pauling's second rule allows two types of local environments of the oxygen atom: three nearest-neighbor B atoms or two B and one C atoms. Only the former type of environment is found in B_4CO_4. This rule is more closely satisfied by B_4CO_4 than the previously proposed B_2CO, explaining why B_4CO_4 is stable and B_2CO is not. Moreover, the computed enthalpy of the reaction

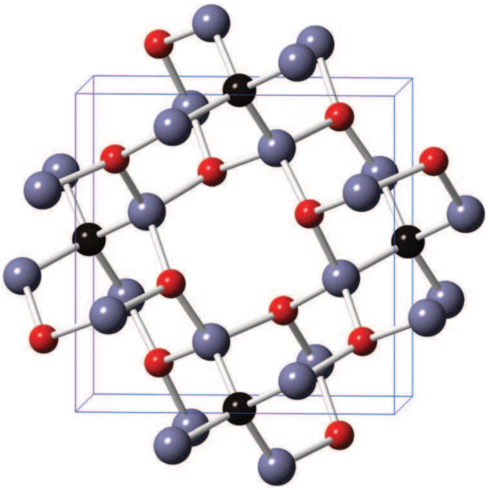

Fig. 2 Structure of B_4CO_4. The purple, black and red balls are boron, carbon and oxygen atoms, respectively.

$$B_2CO + B_2O_3 = B_4CO_4 \tag{1}$$

is negative at all pressures (Fig. 3). For example, at 30 GPa, the enthalpy of this reaction is −0.048 eV per atom.

The dynamical stability was checked by phonon calculations (Fig. S2, ESI†) and to check mechanical stability, we computed the elastic constants (Table S2, ESI†) at ambient pressure. The absence of imaginary frequencies suggests the dynamical stability of B_4CO_4 at ambient pressure. It is well known that mechanical stability of a crystal is typically formulated in terms of strain–stress coefficients (C_{ij} $i,j = 1$–6). The elastic constants matrix must be positive definite

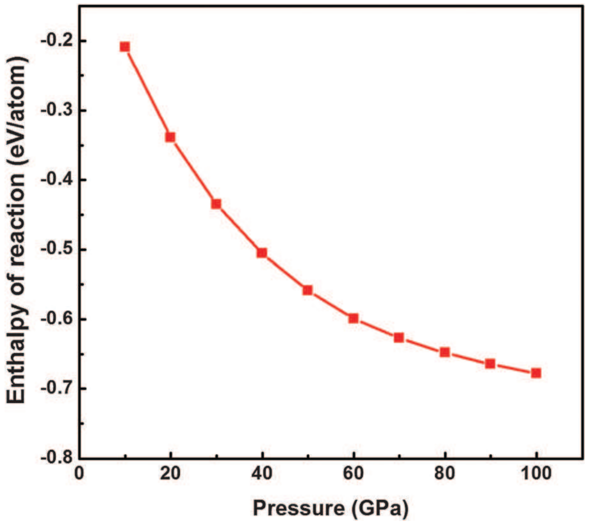

Fig. 3 Enthalpy of reaction $B_2CO + B_2O_3 = B_4CO_4$ as a function of pressure.

because the strain energy must be positive (Born stability criteria).[35] For a tetragonal $I\bar{4}$ crystal, this reduces to four criteria:

$$C_{ii} > 0\ (i = 1, 3, 4, 6);\ (C_{11} - C_{12}) > 0;\ (C_{11} + C_{33} - 2C_{13}) > 0;$$
$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0; \quad (2)$$

The elastic constants of B_4CO_4 (Table S2, ESI†) satisfy the above conditions proving mechanical stability of this material.

Table 1 Hardness (GPa), computed by different models, elastic moduli (GPa), atomic density ρ (atoms per Å^3), Poisson's ratio ν for B–C–O systems at zero pressure

Phases	ρ	B	G	E	$k = G/B$	ν	H_o	H_{chen}
B_4CO_4	0.147	248.1	219.6	508.7	0.885	0.158	38.4	37.6
$B_6C_2O_5$	0.146	228.8	202.6	469.2	0.886	0.158	29.6	35.8
B_2CO_2	0.152	290.7	249.4	581.8	0.858	0.166	41.7	39.2
B_2CO	0.154	276.7	221.1	523.7	0.799	0.185	43.3	33.2
B_6O	0.135	226.4	208.1	477.8	0.919	0.148	31.6	38.1
Diamond	0.175	431.7	519.7	1112.6	1.204	0.0704	89.3	93.4

The hardness of B_4CO_4 was computed using two models: Lyakhov–Oganov model[36,37] and Chen–Niu model.[38] In the Lyakhov–Oganov model, the Knoop hardness is calculated from bond strengths and bond network topology. There are two types of bonds in B_4CO_4 at ambient pressure: B–C bonds (1.570 Å) and B–O bonds (1.505, 1.543, 1.570 Å). Such three-dimensional frameworks of covalent bonds are typical of a superhard material.[39] From Table 1, we can see that the calculated hardness (H_o) is 39 GPa according to the Lyakhov–Oganov model. The bulk modulus (B) and the shear modulus (G) are 248.1 GPa and 219.6 GPa, respectively. We note that all these values are likely to be underestimated due to the known tendency of the GGA to overestimate bond strength and underestimate elastic moduli. From this macroscopic view, the hardness is also calculated based on the Chen–Niu model in which the Vickers hardness is correlated with the shear modulus and Pugh's ratio (G/B). The hardness from the Chen–Niu model (H_{chen}) of B_4CO_4 is 38 GPa. Pugh's ratio is equal to 0.885, indicating that this material is still brittle, but much less so than diamond (1.204).

The electron localization function (ELF) offers a reliable measure of electron pairing and spatial concentration,[40] and has been widely used for analyzing chemical bonding.[41] Fig. 4 shows isosurfaces ELF = 0.85 and, not surprisingly, indicates a covalent interaction between B–C and B–O atoms. The DFT band gap of B_4CO_4 is quite large, 5.30 eV, as a consequence of strongly localized electrons.

Metastable structures are of great significance and in practice can often be synthesized by choosing appropriate precursors and controlling conditions of the experiment (pressure, temperature, quench rate, *etc.*). Here, we report two low-enthalpy metastable phases in the B–C–O system – $B_6C_2O_5$ and B_2CO_2. As is shown in Fig. 5a, in $B_6C_2O_5$, apart from fourfold coordination of B atoms, there exists a single threefold boron atom bonded to two oxygen atoms and one carbon atom; threefold coordination is typical for boron and found, for example, in B_2O_3. At ambient pressure, the average B–C bond length is 1.570 Å, and the average B–O bond distance is 1.534 Å. B_2CO_2 (Fig. 5b) has space group $C2/m$, and its average B–C, B–O, C–C bonds length are 1.643 Å, 1.530 Å and

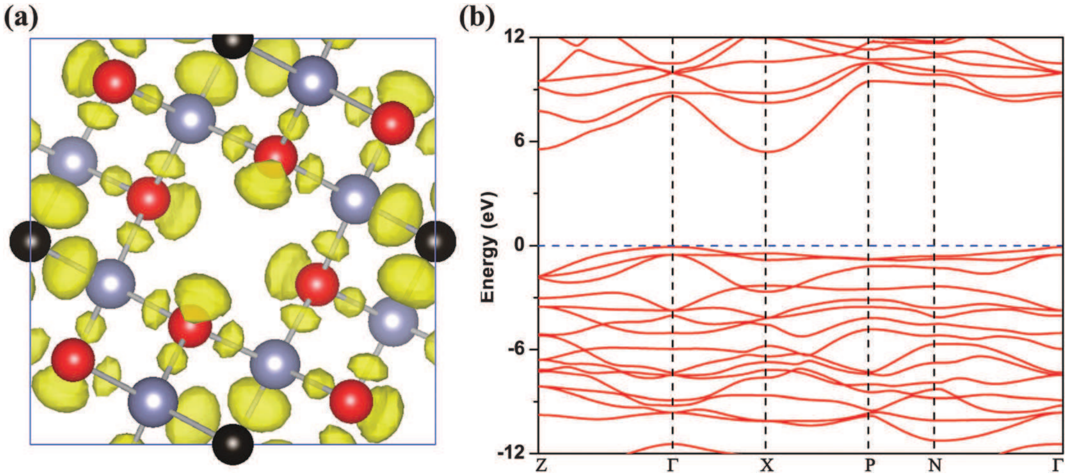

Fig. 4 Electronic structure of B_4CO_4 at ambient pressure. (a) Electron localization function (isosurface ELF = 0.85 is shown), (b) band structure.

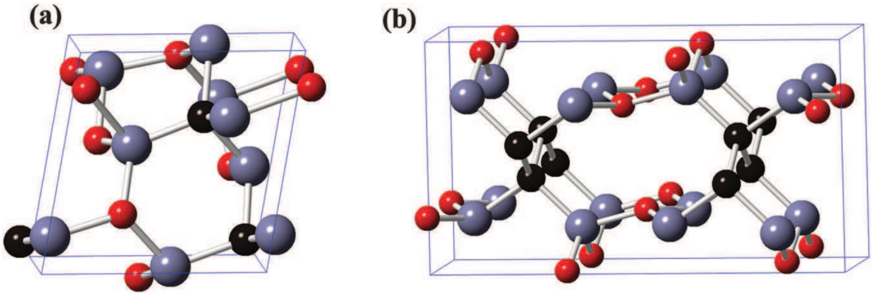

Fig. 5 Structures of metastable phases: (a) $B_6C_2O_5$, (b) B_2CO_2.

1.550 Å, respectively. At 23 GPa, $B_6C_2O_5$ is closest to the convex hull (distances to the convex hull are about 0.045, 0.087 and 0.089 eV per atom for $B_6C_2O_5$, B_2CO_2 and B_2CO). Both $B_6C_2O_5$ and B_2CO_2 are dynamically and mechanically stable at ambient conditions based on the computed phonon dispersions and elastic constants. From Table 1, we can see that their Pugh's ratio is ∼0.88. The calculated Chen–Niu hardness of $B_6C_2O_5$ and B_2CO_2 is 36 GPa and 40 GPa, respectively. As shown in Fig. 6, above 23 GPa, B_2CO and $B_6C_2O_5$ will decompose into B_4CO_4, B_6O and diamond; B_2CO_2 will decompose into B_4CO_4 and diamond.

IV Conclusion

In summary, a systematic search for stable compounds in the B–C–O system at pressures up to 50 GPa has been carried out using the evolutionary algorithm USPEX. Our results reveal a novel stable tetragonal phase – B_4CO_4. Thermodynamically stable at pressures above 23 GPa, B_4CO_4 has a three-dimensional network of covalent bonds, with four-coordinate boron and carbon atoms and three-coordinate oxygen atoms, and theoretical Vickers and Knoop hardnesses around 40 GPa. Apart from B_4CO_4, two new low-enthalpy metastable structures, $B_6C_2O_5$ and B_2CO_2, are found and their hardnesses are around 30–40 GPa. Additionally, all of these compounds remain dynamically and mechanically stable at zero pressure and thus can be quenched to ambient conditions. We hope that this work will stimulate further experimental studies in quest for novel superhard materials.

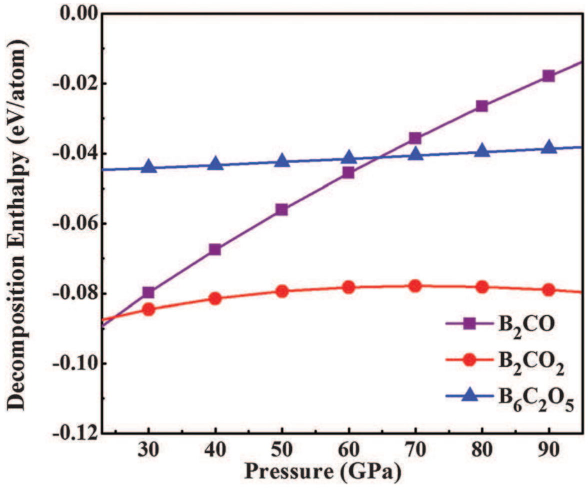

Fig. 6 Decomposition enthalpies for B_2CO ($5B_2CO = B_4CO_4 + B_6O + 4C$), B_2CO_2 ($2B_2CO_2 = B_4CO_4 + C$) and $B_6C_2O_5$ ($5B_6C_2O_5 = 6B_4CO_4 + B_6O + 4C$) as a function of pressure.

Author contributions

S. N. W. performed all the calculations presented in this article with help from Q. Z., G. R. Q., H. F. D. and M. D. E., research was designed by A. R. O. and S. N. W., S. N. W. wrote the paper.

Competing financial interests

The authors declare no competing financial interests.

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References

1 A. Voevodin, S. Walck and J. Zabinski, *Wear*, 1997, **203**, 516.
2 V. Sarin, *Comprehensive hard materials*, Newnes, 2014, vol. 1.
3 J. Musil, *Surf. Coat. Technol.*, 2000, **125**, 322.
4 R. F. Bunshah, *et al.*, *Handbook of hard coatings*, Noyes Publications, New Jersey, 2001.
5 V. Solozhenko, O. Kurakevych and A. R. Oganov, *J. Superhard Mater.*, 2008, **30**, 428.
6 A. R. Oganov, J. Chen, C. Gatti, Y. Ma, Y. Ma, C. W. Glass, Z. Liu, T. Yu, O. O. Kurakevych and V. L. Solozhenko, *Nature*, 2009, **457**, 863.
7 A. R. Oganov and V. Solozhenko, *J. Superhard Mater.*, 2009, **31**, 285.
8 Y. Tian, B. Xu, D. Yu, Y. Ma, Y. Wang, Y. Jiang, W. Hu, C. Tang, Y. Gao and K. Luo, *et al.*, *Nature*, 2013, **493**, 385.

9 Z. Pan, H. Sun, Y. Zhang and C. Chen, *Phys. Rev. Lett.*, 2009, **102**, 055503.

10 L. Vel, G. Demazeau and J. Etourneau, *Mater. Sci. Eng., B*, 1991, **10**, 149.

11 C.-M. Sung and M. Sung, *Mater. Chem. Phys.*, 1996, **43**, 1.

12 A. R. Badzian, *Appl. Phys. Lett.*, 1988, **53**, 2495.

13 D. He, Y. Zhao, L. Daemen, J. Qian, T. Shen and T. Zerda, *Appl. Phys. Lett.*, 2002, **81**, 643.

14 J. Greim and K. A. Schwetz, *Ullmann's encyclopedia of industrial chemistry*, 2000.

15 L. A. Garvie, H. Hubert, W. T. Petuskey, P. F. McMillan and P. R. Buseck, *J. Solid State Chem.*, 1997, **133**, 365.

16 N. Bolotina, T. Dyuzheva and N. Bendeliani, *Crystallogr. Rep.*, 2001, **46**, 734.

17 V. L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar and D. C. Rubie, *Appl. Phys. Lett.*, 2001, **78**, 1385.

18 Y. Li, Q. Li and Y. Ma, *Europhys. Lett.*, 2011, **95**, 66006.

19 C. W. Glass, A. R. Oganov and N. Hansen, *Comput. Phys. Commun.*, 2006, **175**, 713.

20 A. O. Lyakhov, A. R. Oganov, H. T. Stokes and Q. Zhu, *Comput. Phys. Commun.*, 2013, **184**, 1172.

21 A. R. Oganov and C. W. Glass, *J. Phys.: Condens. Matter*, 2008, **20**, 064210.

22 A. R. Oganov, A. O. Lyakhov and M. Valle, *Acc. Chem. Res.*, 2011, **44**, 227.

23 Q. Zhu, D. Y. Jung, A. R. Oganov, C. W. Glass, C. Gatti and A. O. Lyakhov, *Nat. Chem.*, 2013, **5**, 61.

24 Y. Ma, M. Eremets, A. R. Oganov, Y. Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle and V. Prakapenka, *Nature*, 2009, **458**, 182.

25 W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, E. Stavrou, M. Somayazulu, V. B. Prakapenka and Z. Konôpková, *Science*, 2013, **342**, 1502.

26 G. Bergerhoff and I. D. Brown, *Crystallographic Databases, edited by F. H. Allen et al. (Hrsg.) Chester*, International Union of Crystallography, 1987.

27 A. Belsky, M. Hellenbrandt, V. L. Karen and P. Luksch, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 364.

28 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.

29 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.

30 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.

31 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.

32 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671.

33 A. Togo, F. Oba and I. Tanaka, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 134106.

34 Y. Le Page and P. Saxe, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 104104.

35 M. Born and K. Huang, *Dynamical Theory of Crystal Lattices Oxford Classic Texts in the Physical Sciences*, Clarendon Press, Oxford, 1988.

36 K. Li, X. Wang, F. Zhang and D. Xue, *Phys. Rev. Lett.*, 2008, **100**, 235504.

37 A. O. Lyakhov and A. R. Oganov, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 092103.

38 X.-Q. Chen, H. Niu, D. Li and Y. Li, *Intermetallics*, 2011, **19**, 1275.

39 Y. Tian, B. Xu and Z. Zhao, *Int. J. Refract. Met. Hard Mater.*, 2012, **33**, 93.

40 A. Savin, O. Jepsen, J. Flad, O. K. Andersen, H. Preuss and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 187.

41 B. Silvi and A. Savin, *Nature*, 1994, **371**, 683.