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Synthesis of Mg_2C: A Magnesium Methanide[**]

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Carbides, which have been intensively studied for more than half a century, still remain a major center of scientific and technological attention. A large number of new promising phases[1,2] have been predicted to exhibit exceptional structural and electronic properties,[3] as well as high-temperature superconductivity.[4,5] In particular, magnesium compounds containing Mg–C and C–C bonds are quite fascinating from both fundamental science and synthesis perspectives.[6,7] The properties of such compounds are determined by the nature of the chemical bonds present, allowing a variety of different materials to be suggested, such as ionic semiconductors,[8] superhard sp^3 and/or sp^2 carbon networks intercalated with Mg,[7,9] and novel polymeric carbides.[6] Furthermore, the intrinsic nature of Mg–C chemical bonding is of great importance to polar organometallic compounds and to understanding the covalent/ionic nature of carbanions.[10,11]

The ambient-pressure chemistry of the Mg–C system was studied quite thoroughly in the past.[12] Magnesium forms an acetylide-type carbide, MgC_2,[13] similar to all other alkaline-earth metals. Mg also forms Mg_2C_3,[14] a derivative of propadiene ($H_2C{=}C{=}CH_2$), which is unique for the alkaline-earth metals and is one of only a handful of examples that contain the rare $[C{=}C{=}C]^{4-}$ group. Herein, we present the formation of a third carbide of magnesium, namely Mg_2C. This compound is stabilized at pressures above 15 GPa, but is fully recoverable to ambient conditions and contains the very unusual C^{4-} methanide anion.[12,15]

Both in situ and ex situ X-ray diffraction experiments revealed the formation of magnesium carbide, Mg_2C, directly from a stoichiometric mixture of the elements at pressures between 15–30 GPa and temperatures of 1775–2275 K (Figure 1). Samples were recovered in powder form, which have a brown color, and Rietveld analysis indicates that the compound takes on the antifluorite structure (Li_2O) in the cubic crystal system with space group $Fm\bar{3}m$ (No. 225) with lattice parameter $a = 5.4480(4)$ Å.

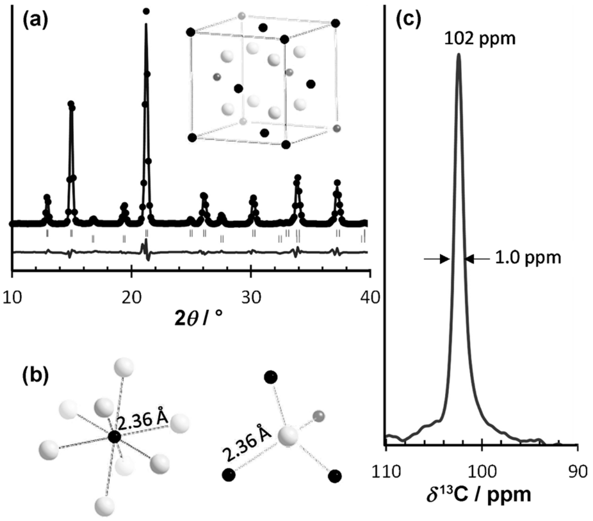

Figure 1. a) X-ray diffraction data with Mo K_α radiation (●), Rietveld refinement (——), and difference (at bottom). Tick marks are shown for Mg_2C (top) and MgO impurity (bottom). b) Carbon and magnesium coordination in Mg_2C. c) NMR spectrum of $Mg_2{}^{13}C$ (99% of isotope purity).

A comparison of local bonding environments (structural coordination) for Mg_2C is presented in Figure 1b. Contrary to Mg_2C_3 and MgC_2, Mg_2C does not contain covalent C–C bonds. According to our structural data, the ambient-pressure Mg–C distance in Mg_2C (2.36 Å) is larger than the minimal Mg–C distances in both Mg_2C_3 (2.21 Å) and MgC_2 (2.17 Å) and smaller than the Mg–C distance in Al_2MgC_2 (2.487),[16] where Mg has octahedral coordination. Carbon within Mg_2C is coordinated eightfold by magnesium, whereas carbon coordination within Mg_2C_3 and MgC_2 is much more sophisticated. If the whole carbon anions are considered as structural units, Mg_2C_3 and Mg_2C have the same coordination number 8, but in the first case they form a distorted and elongated dodecahedron, while in the second case the coordination polyhedron is a regular cube. In MgC_2 the C_2 dumbbell coordination number is 6 (elongated octahedron).

Among the Group 2 elements, beryllium forms the only known methanide-type carbide. Be_2C, as well as a second known methanide, Al_4C_3, are quite hard, low-compressibility compounds with a large degree of covalent bonding character (the ionic/covalent nature is described below). The minority phase synthesis of Li_4C was reported previously, but minimal yields (0–10%) have precluded definitive characterization.[12] Although never experimentally observed until now, the isostructural magnesium analogue of Be_2C, namely Mg_2C, was first suggested by Corkill and Cohen[8] about twenty years

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ago and studied using ab initio methods.[17] Mg_2C was assumed to take on the antifluorite structure and was predicted to be a highly ionic compound with a narrow indirect bandgap of about 1 eV.

The ^{13}C NMR spectrum (Figure 1 c) of $Mg_2{}^{13}C$ sample (99 % of isotopic purity) displays one resonance at δ, +102 ppm. This agrees with the antifluorite structure, which contains only one unique crystallographic position for carbon. The chemical shift is significantly higher than that of C^{4-} in Al_4C_3 (34 and 51 ppm for C atoms in two crystallographically different sites),[18] and agrees well with higher degree of covalent character of Al−C bonding as compared with Mg−C. The absence of J coupling in the observed NMR spectrum suggests that carbon within the compound is primarily ionic; increased covalency would be manifested by the presence of J coupling.[19]

Similar to other known magnesium carbides, the Mg_2C compound is easily hydrolyzed by the moisture in air. Samples must be handled cautiously within an inert atmosphere to avoid hydrolysis. Using gas chromatography (GC) analysis (Supporting Information, Figure S8) with an Ar carrier stream, we observed methane, CH_4, as the only product of hydrolysis according to the reaction $Mg_2C + 4H_2O \rightarrow 2Mg(OH)_2 + CH_4$. The formation of methane confirms the presence of the C^{4-} anion in the crystal structure, which may be viewed as a strong Lewis base.

The formation of Mg_2C from the elements indicates the thermodynamic stability of this phase at pressures above 15 GPa; that is, stabilization relative to the elements by the pV contribution to the free energy. In our experiments at 9 GPa, formation of Mg_2C was not observed, but a phase with a powder diffraction pattern similar to Mg_2C_3 was recovered in some experiments.

To further elucidate the thermodynamic stability of Mg_2C, we performed density functional theory (DFT) calculations to determine formation enthalpies with pressure. Starting from 15 GPa (at 0 K) Mg_2C becomes stable as compared to the elements (Figure 2 a), and it is the only stable compound on the convex hull up to 50 GPa. Assuming ambient pressure structures, Mg_2C_3 and MgC_2 never become thermodynamically stable with respect to Mg_2C and disproportionation into the elements, although different high-pressure structures may be possible. Our calculations were referenced to a mixture of diamond and hcp magnesium (graphite reference shown in Supporting Information). Formation enthalpies of MgC_2 and Mg_2C_3 at ambient pressure were reproduced within 20 % of experimental uncertainty using this approach.[20,21] However, it is also interesting to note that while Mg_2C_3 and MgC_2 are both thermodynamically metastable, they can be formed through several types of synthesis reactions.

The calculated dynamic stability of Mg_2C outside the thermodynamic stability field, that is, absence of imaginary frequencies down to ambient pressure (Figure 2 b, inset), is consistent with the experimentally observed ambient-pressure recoverability.

The experimental equation of state (EoS) of Mg_2C up to 33 GPa at 300 K and corresponding p–V relationship calculated by DFT are presented in Figure 2 b. Fitting of the experimental data to a third-order Birch–Murnaghan equation leads to a bulk modulus $B_0 = 87(1)$ GPa with pressure derivative $B'_0 = 5.1(3)$ and zero-pressure unit cell volume $V_0 = 161.70(2)$ Å^3. The bulk moduli for Group 2–14 antifluorite compounds can be estimated from the semiempirical equation $B_0(\mathrm{GPa}) = 1846\ d(\text{Å})^{-3.5}$, where d is the average nearest neighbor distance.[8] It is interesting to note that this equation gives $B_0 = 91$ GPa, which very close to our experimental value. It is also interesting to compare Mg_2C with its lighter and remarkably less compressible analogue Be_2C, which has $B_0 = 220$ GPa (or 205 GPa according to the semiempirical equation just mentioned).

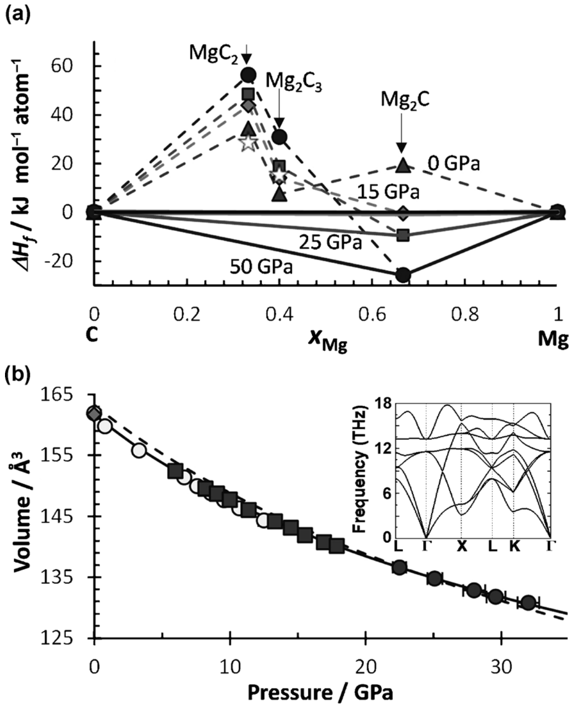

Figure 2. a) Formation enthalpies of MgC_2, Mg_2C_3, and Mg_2C at different pressures (DFT, 0 K). Solid lines connect stable structures along the convex hull. Dashed lines connect all phases at a given pressure. Open stars represent experimental data. b) Experimental equation of state of Mg_2C (——) compared with DFT (-----). Different symbols indicated different experimental runs. Inset: phonon dispersion in Mg_2C (DFT, 0 K, 1 MPa). Absence of imaginary frequencies at ambient pressure confirms dynamic stability.

Our DFT calculations provide an EoS that is in excellent agreement with the experimental data, showing an average absolute deviation of only 0.8 %. These calculations provide EoS parameters ($B_0 = 89.9$ GPa, $B'_0 = 4.02$, and $V_0 = 163.3$ Å^3) that are in much better agreement with experiment than those previously reported for Mg_2C,[8,17,22] and should serve as a basis for the calculation of more realistic electronic and optical properties. The ambient-pressure DFT (PBE) indirect (direct) bandgap of 0.67 eV (1.34 eV) calculated here is notably lower than those reported previously: 0.77 eV (1.8 eV)[17] and 0.97 eV (ca. 1.9 eV).[8]

The nature of interaction between carbon and magnesium can, to some extent, be rationalized by examining differences in electronegativity. For the case of beryllium (the only known alkaline earth metal structural analogue of Mg_2C), the

Pauling electronegativity[23] difference between beryllium and carbon is lower ($\Delta\chi = 0.98$) than the difference between carbon and magnesium ($\Delta\chi = 1.55$). For more detailed analysis it is better to use the so-called covalence degree $\beta = 4\chi^2_{\text{cation}}/(\chi_{\text{cation}}+\chi_{\text{anion}})^2$.[24] For Be_2C, $\beta = 0.58$; that is, $\beta > 0.5$, as is the case for boron nitride BN ($\beta = 0.64$) and Si_3N_4 ($\beta = 0.59$), typical covalent compounds with partially ionic bonds. At the same time, the isostructural magnesium compound is predominantly ionic with $\beta = 0.46$, that is, $\beta < 0.5$ like in the case of other typically ionic compounds, such as BeO ($\beta = 0.39$) and MgI_2 ($\beta = 0.44$). This fact agrees well with the higher compressibility of Mg_2C ($B_0 = 87$ GPa) as compared to the remarkably more covalent Be_2C ($B_0 \approx 220$ GPa)[8] and Al_4C_3 ($B_0 = 120$ GPa).[25] The ionic bonding character also explains the high reactivity of Mg_2C with water (almost instantaneous in air) as compared to Be_2C that may resist even diluted acids. The high ionic character should also influence the mechanical properties. For example, the Vickers hardness of Mg_2C, estimated using a thermodynamic model of hardness,[24] gives $H_V = 7.7$ GPa, while for covalent Be_2C, the theoretical value is $H_V = 18$ GPa versus 24 GPa measured experimentally (Knoop hardness value H_K).

To gain further insights into the ionic chemical bonding, we calculated the electron density in the structure and performed a Bader-type bonding analysis (Figure 3). These results confirm the highly ionic nature of the solid: the effective charges on Mg and C are +1.57 and −3.14, respectively. To our knowledge, this is the most negative effective charge of carbon ever achieved (for comparison to other compounds, see Ref. [15]), while the C^{4-} ionic radius in Mg_2C has the highest value of 1.50 Å. The magnesium charge is the lowest among other known carbides (+1.65 and +1.7 for Mg_2C_3 and MgC_2, respectively). The charge density in the (110) plane shows a nearly spherical distribution of electrons centered at Mg and C ions with a low electron density in the interstitial regions (Figure 3a). The electron localization function (ELF, Figure 3b) provides a closer look at the bonding nature. ELF minima observed between Mg and C atoms confirm the closed-shell ionic nature of the bonding. There is no "shared-electron" picture, which is characteristic of covalent bonding and requires ELF maxima between atoms.

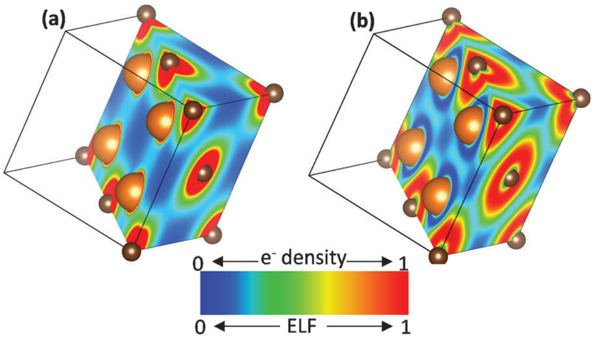

Figure 3. a) Normalized electron density distribution in Mg_2C, colored blue to red (scale 0 to 1). b) Electron localization function (ELF). Delocalized to localized electrons colored from blue to red (scale from 0 to 1). Small and large spheres represent carbon and magnesium, respectively.

In summary, we have successfully synthesized the previously hypothesized magnesium carbide, Mg_2C, for the first time. As predicted, the structure, which is fully recoverable to ambient pressure, takes on that of antifluorite. The compound contains unusual C^{4-} anions, which is extremely rare for alkaline-earth-metal carbides, and the isolation of this ion in the truly ionic environment afforded by Mg_2C helps to clarify the nature of bonding between these two elements. The anionic nature of the methanide ion allows for easy hydrolysis. Our results highlight the unique role of carbon in forming structures with varied orbital hybridizations, as well as the uniqueness of magnesium, which is now known to form three different carbide phases with three different carbon anions.

Experimental Section

Commercially available powders of magnesium (Sigma–Aldrich, −325 mesh, 99.5%) and glassy carbon (Aldrich, spheric powder 2–12 μm, 99.95%) or graphite (Aldrich, synthetic powder, < 20 μm) were used. The powders was degasified over 12 h at about 200 °C in a vacuum oven and then sealed in Ar. Typical powder XRD pattern shows that Mg is a well-crystalline phase, while broad and asymmetric reflections of glassy carbon indicate a highly disordered (amorphous) structure. The initial mixture (Mg:C = 2:1) was ground in a porcelain mortar in the Ar glovebox to ensure homogeneous mixing. The sample preparation in air may lead to noticeable amounts of MgO in the product, but generally does not influence the synthesis conditions and formation of the Mg_2C phase. For large-volume synthesis, the precompressed tablets of Mg/C mixture were introduced into high-pressure cell, that is, octahedral-shaped assembly for multi-anvil (14/8 type, pressures up to 15 GPa; Supporting Information, Figure S1) and compressed to the desired pressure (15 GPa). The heating was typically performed during 30 min at 1770–2000 K. After that, the temperature was decreased by switching off the power. Diamond anvil cell syntheses (up to 30 GPa and 2200 K with XRD in situ probing; Supporting Information, Figure S1) were performed at HP-CAT, sector 16, at the Advanced Photon Source facility using laser heating. A small amount of powder (either mixture or Mg and C layers) was loaded within a rhenium gasket in a diamond anvil cell equipped with 300 μm culet diamonds. Different pressure media were employed (Ne, LiF, KCl) to assure the thermal isolation from diamonds and quasi-hydrostatic conditions for subsequent in situ measurements. Pressure has been estimated using the pressure medium equation of state (Ne, LiF, or KCl) in the vicinity of sample, as well as a ruby gauge. The zero-pressure volume has been fixed to that of sample recovered from multianvil experiments. To generate high temperatures, samples were heated on both sides using an IR fiber laser. In some cases two or three heating cycles were performed, with X-ray diffraction patterns collected before, during, and after laser heating. Usually we observed very good agreement between pressures measured before and after heating. During laser heating, temperatures from each side of the heated sample were measured by collecting emitted radiation between 600 and 800 nm, correcting for the optical system response and fitting the spectral data to Planck's equation assuming constant emissivity. Details of X-ray characterization, ab initio methods, NMR and gas chromatography can be found in the Supporting Information.

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