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FAST TRACK COMMUNICATION

Synthesis of novel Ru₂C under high pressure–high temperature conditions

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Abstract

We report here, for the first time, synthesis of the Fe₂N type hexagonal phase of ruthenium carbide by a high pressure–high temperature technique using a laser heated diamond anvil cell (LHDAC). The synthesis is carried out by laser heating a mixture of pure elements, Ru and C, at very low ‘pressure’ of 5 GPa and $T \sim 2000$ K. The structure of the temperature quenched high pressure phase is characterized by *in situ* high pressure x-ray diffraction (HPXRD) and is corroborated by *ex situ* TEM imaging and diffraction, carried out for the first time on the retrieved sample synthesized by LHDAC. The lattice parameters of Ru₂C at ambient pressure are found to be $a = 2.534$ Å and $c = 4.147$ Å. *In situ* HPXRD studies up to 14.2 GPa yield a bulk modulus of 178(4) GPa. Electronic structure calculations reveal the system to be metallic in nature with a degree of covalence along the Ru–C bond. As ruthenium is isoelectronic to osmium, this result for Ru₂C has significant implications in the synthesis and study of osmium carbides.

(Some figures may appear in colour only in the online journal)

Transition metal (TM) carbides and nitrides have many industrial applications due to their high hardness, high melting point, excellent thermal conductivity, good wear and corrosion resistance [1]. The exploration of novel phases of TM carbides and nitrides is an alternative route in the quest for super hard materials as compared to systems formed with low atomic number (Z) elements like cubic boron nitride [2–4]. The essence of this approach is to have maximum valence electron charge density, basically contributed by the TM, and forming a p–d hybridized covalent bond between C and TM respectively. Among TMs Os is the least compressible and has the highest valence

electron charge density of 0.572 electrons Å⁻³. Due to the wide ranging interest in these systems, several electronic structure calculations have been carried out to understand the stability and structural properties [5–9]. It is observed that the formation energies (enthalpy of formation) of carbides and nitrides of the later TMs are positive and low compared to those of the early TMs and hence they are not easily formed. For example, the carbides of Ir, Rh, Pd etc have not yet been synthesized. As pressure is known to change the electronic structure considerably and enhance the chemical reactivity of elements, it may be possible to synthesize these novel carbides and nitrides under high pressure–high temperature conditions, which otherwise are not possible by the conventional methods. Recently, high pressure synthesis of PtC [10], Re₂C [11], IrN₂, OsN₂ [12], Re₂N and Re₃N [13] have been reported. RuC has been reported to be synthesized

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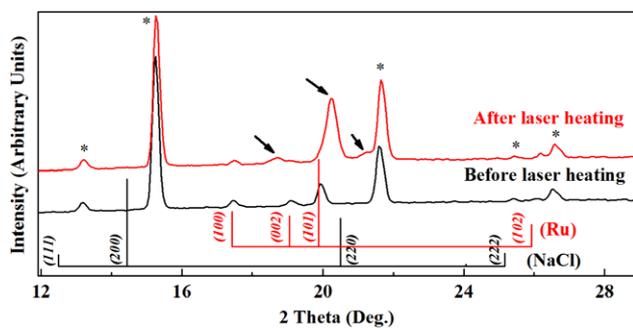


Figure 1. HPXRD plots showing the synthesis of ruthenium carbide after laser heating pure Ru + C at 5 GPa. The arrows indicate peaks belonging to the newly formed ruthenium carbide phase and * denotes NaCl peaks at 5 GPa. The tick plots for Ru and NaCl are at ambient pressure.

by inductive heating of the elements in an inert atmosphere in the hexagonal phase which is isomorphous to WC with very high micro-hardness [14]. However, the above result has not yet been reproduced. As Ru is isoelectronic to Os, it would be interesting to study the formation of ruthenium carbide by the high pressure synthesis technique, the structure it adopts and its stability regime.

A laser heated diamond anvil cell (LHDAC) facility setup in our lab is used to carry out high pressure–high temperature synthesis experiments [15]. The LHDAC setup consists of a Mao-Bell type diamond anvil cell (DAC) into which a CO₂ ($\lambda = 10.6 \mu\text{m}$, 120 W, CW mode) laser beam is focused to heat the sample. The DAC is mounted on a XYZ- θ stage, in which the motion along the X–Z directions is brought about by two computer controlled nanomovers. By the controlled movement of the stages, various regions of the sample can be brought into focus with the laser beam. Heating of the sample is monitored by a CCD based imaging system. Sample assembly for the LHDAC experiment is crucial and has to be optimized for efficiently converting the incident IR beam into heat concentrated on the sample without much dissipation. A stainless steel gasket is preindented to a thickness of $\sim 80 \mu\text{m}$ and a through hole of diameter $\sim 150 \mu\text{m}$ is drilled at the centre. This is completely filled with NaCl and pressed for compaction. A small pit is scooped in the NaCl layer into which a pelletized sample of size $\sim 100 \mu\text{m}$ is mounted. The sample is then covered with a layer of NaCl and compacted. NaCl acts as a good thermal insulator, an IR window, pressure transmitting medium and is also used for pressure estimation. The sample assembly is standardized by including an optimum ratio of ruthenium and graphitic carbon, both 99.9% pure. This is important, as a sufficient quantity of C is required which predominantly couples with the laser for good sample heating. Similarly, a smaller quantity of Ru may lead to synthesis of a novel phase with very low volume fraction and may not be deciphered from XRD measurements. Towards this end, many trial runs were carried out with different ratios of Ru and C and we found the optimum ratio of Ru:C to satisfy the above requirements to be 1:4. Temperature measurement is done by the spectroradiometric technique [16]. In this technique the

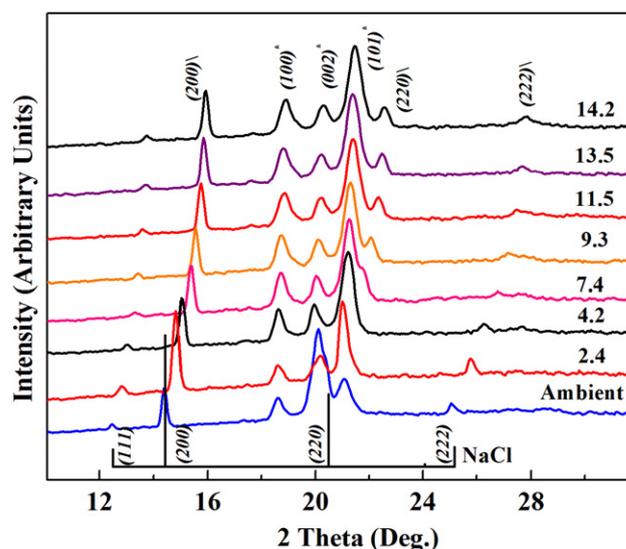


Figure 2. HPXRD plots of the novel Ru₂C at ambient temperature. The numbers on the right indicate pressure in GPa. The peaks labelled with * are of the carbide phase and unlabelled peaks are that of NaCl.

black body radiation spectrum of the hot microscopic sample is recorded using a CCD based spectrometer, and temperature is estimated by fitting the thermal spectra with Planck's law or using Wien's law. The equation of state (EOS) for NaCl is used to estimate pressure [17]. The laser heated samples are characterized by a high pressure x-ray diffraction (HPXRD) technique in angle dispersive geometry. The incident Mo K α_1 x-ray beam is obtained from a 18 kW rotating anode x-ray generator. The diffracted beam is collected by an image plate based *mar345dtb* giving an overall resolution of 0.001 Å.

Ru:C in the ratio 1:4 is loaded into the DAC and pressurized to ~ 5 GPa. The CO₂ laser is focused to a spot size of $\sim 40 \mu\text{m}$ to heat the sample. A persistent glow seen on the sample indicates that the coupling of the laser to the sample is very good. The temperature of the hot microscopic sample is found to be ~ 2000 K. In figure 1, the HPXRD pattern before laser heating contains intense Bragg peaks of ruthenium and that of NaCl. After laser heating the sample we observe a significant reduction in intensity of all the Ru peaks. Associated with this, the appearance of new peaks at 18.67°, 20.22° and 21.23° is observed. This signifies consumption of ruthenium in the formation of carbide. The HPXRD pattern of the high pressure phase does not match with the earlier reported RuC in hexagonal phase [13]. The sample cell is then taken to higher pressures (up to 14.2 GPa) to study the structural stability and also the compressibility behaviour of the novel phase formed. Figure 2 shows the HPXRD patterns of the novel phase as a function of pressure at ambient temperature. The ambient pattern shown in figure 2 is obtained in the reverse cycle and it is seen that the high pressure synthesized phase is retained at ambient pressure. At lower pressures, there is overlap of the NaCl(220) peak with an intense peak of the high pressure synthesized phase, which clearly gets separated above 7.4 GPa. The HPXRD pattern at 14.2 GPa is considered for the determination of the

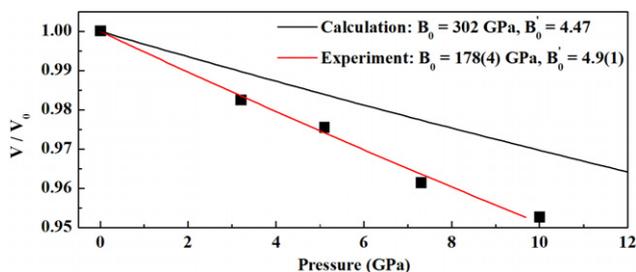


Figure 3. Experimental and calculated P–V data of Ru₂C fitted with the Birch–Murnaghan equation of state.

crystal structure. At this pressure, the 2θ peak positions of the high pressure synthesized phase are 18.89° , 20.25° and 21.43° . Lattice determination is carried out using powder data interpretation and indexing (POWD) [18], and a hexagonal lattice with $a = 2.495 \text{ \AA}$ and $c = 4.035 \text{ \AA}$ is obtained with a very good figure of merit ($F = 84.2$). The ambient lattice parameter is found to be $a = 2.534 \text{ \AA}$, $c = 4.147 \text{ \AA}$ and $V = 23.05 \text{ \AA}^3$. The P–V curve for the new phase is shown in figure 3 and Birch–Murnaghan equation of state is used to fit the P–V data. Bulk modulus and its pressure derivative obtained are $178(4) \text{ GPa}$ and $4.9(1)$ respectively.

The Mao–Bell DAC has a limited 2θ opening which imposes constraints in probing small d values and the retrieved sample quantity is too small to take normal XRD. TEM characterization will enable us to probe a larger d range compared to the XRD studies. A high pressure synthesized sample is retrieved from DAC wherein NaCl is used as the pressure transmitter/thermal insulator. Thus NaCl is manually separated from the sample. The sample is then mounted between diamond anvils and sheared. This is done so as to obtain some significant portion of thin crystallites which are transparent to electrons. The sample quantity obtained is not enough to disperse in methanol for subsequent pouring onto a carbon coated copper grid to observe the particles under a transmission electron microscope. Hence, the sheared sample is transferred on a carbon coated copper grid on which deionized water is placed drop by drop to dissolve residual NaCl. The samples as prepared above are imaged under diffraction contrast conditions with a JEOL JEM 2000 EX II transmission electron microscope operating at 200 kV accelerating voltage and the diffraction patterns are recorded at 100 cm camera length. The images and the diffraction patterns are calibrated with the standard microscope calibration data obtained from the standard Au sample and are analysed by Image J. The bright field image and the diffraction pattern from the ruthenium carbide sample are given in figure 4.

It is observed that the particles are agglomerated as they are not ultrasonicated and dispersed onto the grid before microscopy observation. The particles are mostly faceted and the sizes of the particles vary from 100 to 500 nm. In the diffraction pattern, a number of almost continuous Debye–Scherrer rings can be observed. Some incomplete rings can also be seen decorated with localized bright spots. The discontinuous Debye–Scherrer rings are due to the small

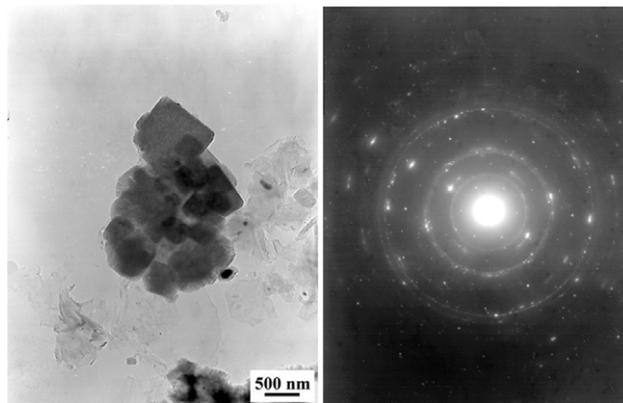


Figure 4. TEM bright field image and diffraction pattern from the ruthenium carbide sample.

number of crystallites present in the sample. Apart from the reflections seen in the HPXRD patterns, five more interplanar spacings are seen in the extended d -range of $3.5\text{--}0.7 \text{ \AA}$ in the electron diffraction pattern. The d spacings observed in the diffraction patterns are given in table 1. Micro-Raman measurements have also been carried out on the retrieved sample. No Raman modes apart from diamond like carbon features were observed.

Solving the crystal structure of the novel phase obtained in the LHDAC based experiments is a nontrivial task, since (i) few interplanar spacings are obtained in HPXRD experiments, (ii) there are preferred orientation effects, (iii) the volume fraction is very low to carry out normal XRD on the retrieved sample and (iv) the presence of un-reacted starting elements leads to difficulty in the estimation of stoichiometry. To arrive at the possible list of candidate structures, a survey on the phase diagrams of the existing TM carbides is carried out. It is seen that mono-carbides of group IVa, Va and VIa adopt a cubic lattice with the exception of MoC and WC, which are found in hexagonal lattices. Theoretical diffraction patterns were generated for MoC and WC structure types but they do not correspond to the experimental pattern. The formation energy for RuC and Ru₂C is estimated to be $+26$ and $+15 \text{ kJ mol}^{-1}$ of atoms respectively [19] and also in group VIIa and VIII carbides, the ratio of metal to carbon is greater than one, signifying that the formation of Ru₂C is thermodynamically more favourable than RuC. Recently hexagonal rhenium carbide (Re₂C) has been reported by high pressure synthesis [12]. In view of these facts, a closer look at the phase diagram of TM carbides of the type TM₂C reveals that these systems predominantly adopt the following space groups: $P3_121$ (152), $P\bar{3}m1$ (164), $P\bar{6}m2$ (187) and $P6_3/mmc$ (194). While indexing the observed new peaks with POWD, the space group $P3_121$ is ruled out as the intense peak of the high pressure phase is left unindexed. Also, space group $P\bar{6}m2$ yields a very low figure of merit of 1.9. This leaves us with two options: $P\bar{3}m1$ and $P6_3/mmc$ space groups, which are to be evaluated.

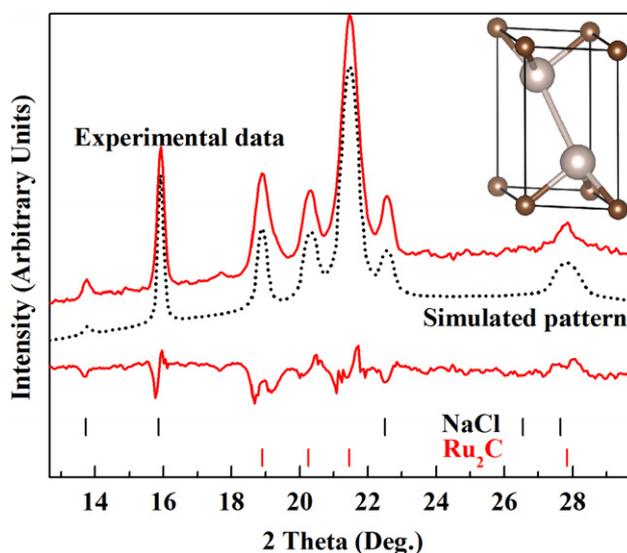
At this stage, we use electronic structure calculations to fix the space group. The electronic structure calculation is carried out for these two possible space groups. The full

Table 1. List of the d -spacings (at ambient pressure) observed in electron diffraction experiments along with the calculated values for the space group $P\bar{3}m1$ (164). * PDF (No. 05-0628) for NaCl and # PDF (No. 06-0663) for Ru of ICDD, USA.

TEM observed d (Å)	Calculated d (Å) for Ru ₂ C	d (Å) for NaCl *	d (Å) for Ru #	Remarks
3.46		3.26		From NaCl only
2.84		2.82		From NaCl only
2.14	2.19		2.14	Mainly from Ru ₂ C
2.06	2.07		2.05	Mainly from Ru ₂ C
2.01	1.94	1.99		Mainly from Ru ₂ C
1.54	1.51	1.62	1.58	Mainly from Ru ₂ C
1.43		1.38	1.35	From Ru and NaCl
1.27	1.27			From Ru ₂ C only
1.24		1.26	1.22	From Ru and NaCl
1.16	1.17			From Ru ₂ C only
1.07	1.08			From Ru ₂ C only
0.91	0.86		0.90	Mainly from Ru ₂ C
0.71	0.71		0.71	Mainly from Ru ₂ C

potential linear augmented plane wave (FP-LAPW) method as implemented in WIEN2k code [20] is used to calculate the total energy and the electronic structure of Ru₂C in both the space groups. The band structure and the density of states are calculated using 1000 k -points in the irreducible Brillouin zone (IBZ) for the non-magnetic state. An improved version of generalized gradient approximation [21] (GGA-PBE96) is used. The plane-waves with a cut off of $RMT * K_{max} = 10$ are used, where RMT denotes the smallest atomic sphere radius and K_{max} is the magnitude of the largest k -vector in the plane wave expansion. We have first considered $P6_3/mmc$ (space group 194). However, with relaxed lattice parameters this structure model predicts a cell volume of 60 \AA^3 which does not correspond with the experimentally determined volume. Next, the hcp structure ($P\bar{3}m1$, space group No:164) as seen in the Fe₂N type structure is considered and the calculations are performed. In this case, the calculated lattice parameters match reasonably well with the experimental values. The calculated lattice parameters obtained are: $a = 2.8849 \text{ \AA}$ and $c = 4.8769 \text{ \AA}$ with a cell volume of 35.15 \AA^3 . The simulated pattern for Ru₂C (SG 164) with Fe₂N structure type is shown in figure 5. The calculated and experimentally obtained XRD patterns match very well. Moreover, the list of d -spacings predicted by the Fe₂N structure type agrees well with that obtained in the XRD and TEM measurements (table 1). It is thus clearly seen that the structure of the novel Ru₂C phase formed is hexagonal Fe₂N structure type with space group $P\bar{3}m1$ (164). A unit cell of Ru₂C is shown in the inset given in figure 5.

The computed bulk modulus of Ru₂C is 302 GPa, whereas experimentally it is found to be 178 GPa. It is interesting to note here that the large difference between the experimental and theoretical values of bulk modulus have also been reported for the high pressure synthesized group VIII nitride IrN₂ [12]. The lattice parameters and physical properties of TM carbides are strongly correlated with stoichiometry and TMs are well known to form in non-stoichiometric compounds. Simulations of off stoichiometry effects on lattice parameters show 10–15% change in the Re–C system [22]. Here, it may be noted that the bulk

**Figure 5.** Experimental and simulated XRD plots for Ru₂C + NaCl. Inset: unit cell of Ru₂C, the corner atoms are C and two Ru atoms are at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4) respectively.

modulus of elemental Ru is quite high (320 GPa) compared with the experimental as well as computed values for Ru₂C 178 GPa and 302 GPa respectively. First principle calculations on OsC, Os₂C₃ and OsC₂ in cubic and hexagonal structures have been reported [23]. It is seen that bulk moduli in these systems vary between 245 and 383 GPa which are significantly lower than the reported bulk modulus of 405 GPa for elemental Os [24]. Thus the calculated bulk modulus for Ru₂C seems to be in the same range as for the other similar systems, but the large discrepancy between the calculated and experimental values still remains inexplicable. The density of states (DOS) and the band structure for Ru₂C are shown in figure 6(a) and the electronic charge distribution on the (110) plane is shown in figure 6(b). The DOS at E_F is mostly dominated by the d -states of Ru. From the DOS plot Ru₂C is found to be metallic in nature. This can be compared with the Os–C system where it is seen that hexagonal OsC₂ is metallic whereas cubic OsC is seen to be semiconducting [23]. In figure 6(b) the corner atoms are C and the nearest C–C

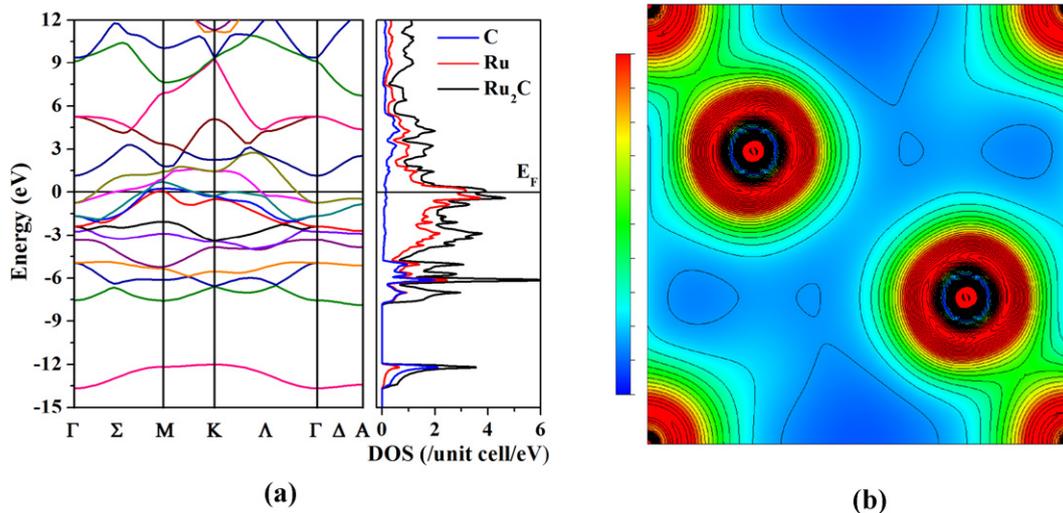


Figure 6. (a) Electronic band structure and DOS plots for Ru_2C with space group $P\bar{3}m1$, (b) electronic charge distribution on the (110) plane (maximum intensity shown in red corresponds to $1.33 \text{ electrons } \text{\AA}^{-3}$), the corner atoms are C.

distance is 2.553 \AA . There is very low charge density between the C atoms and a signature of covalence is seen between Ru and C.

Recently, a semi-empirical method has been proposed to estimate hardness from the structural details [25, 26]. The expression for hardness with systems having two bond strengths is given as $H = (C/\Omega)2(b_{12}s_{12}b_{34}s_{34})^{1/2} e^{-\alpha f}$, where C and α are constants (1450 and 2.8 respectively) and Ω is the volume of the unit cell. s_{12} and s_{34} are bond strengths given by the expression $s_{ij} = (e_i e_j)^{1/2} / n_i n_j d_{ij}$, where e_i is the valence electron charge density given by $e_i = Z_i/R$, Z_i is the valence electron number and R is the atomic radius. In the case of ruthenium we have used $Z = 6$ as suggested for heavy TMs by Simunek *et al* [26]. From the structure obtained for Ru_2C , the following values are used in computing hardness: the number of bonds $b_{12}(\text{Ru}-\text{C}) = 6$ and $b_{34}(\text{Ru}-\text{Ru}) = 1$; the bond distances $d_{12} = 1.7967 \text{ \AA}$; $d_{34} = 2.5292 \text{ \AA}$ respectively. Each C is coordinated by six Ru at d_{12} ($n_1 = 6$) and Ru is coordinated by 12 Ru atoms ($n_2 = n_3 = n_4 = 12$) at distance d_{34} . With this semi-empirical model, we estimated hardness to be 6.26 GPa. For TM carbides the estimated hardness value of Ru_2C is low. This can be understood from the unit cell of Ru_2C shown in figure 5, the structure can be thought of as two layers of ruthenium atoms stacked between two carbon layers and the electronic charge distribution shown in figure 6(b) suggests the bonding to be metallic between the Ru layers. This implies a very low shear modulus for Ru_2C . Also, the ratio of metal to carbon is reported to be directly related to shear and bulk modulus, signifying that metal carbon bonds withstand larger stress [23]. In Ru_2C , the metal to carbon ratio is 0.5, and this may be the possible reason for the nominal hardness value estimated.

In summary, Ru_2C has been synthesized for the first time by the high pressure–high temperature route using the LHDAC technique. With respect to other carbides, ruthenium carbide is formed at a moderate pressure of 5 GPa, which is easily achievable with multianvil cell apparatus. Multianvil

cell synthesis will result in a bulk quantity of the novel phase thereby enabling complete structural and mechanical characterization. *In situ* HPXRD and electronic structure calculations on the novel phase have been carried out. Also the sample retrieved from LHDAC has been studied for the first time by the electron diffraction technique. The structure of the novel phase has been found to be Fe_2N type hexagonal with space group $P\bar{3}m1$. *In situ* HPXRD studies up to 14.2 GPa yield a bulk modulus value of 178(4) GPa. Electronic structure calculations reveal the Ru_2C system to be metallic in nature. It is suggested that osmium carbide may adopt crystal structures as seen in Re nitride and carbide systems [13]. However, as osmium is isoelectronic to ruthenium one would expect similar trends to those seen in ruthenium carbide.

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References

- [1] Toth L E 1971 *Transition Metal Carbides and Nitrides* (New York: Academic) and references cited therein
- [2] Brazhkin V V, Lyapin A G and Hemley R J 2002 *Phil. Mag. A* **82** 231
- [3] Chandra Shekar N V and Sahu P Ch 2008 *Indian J. Phys.* **82** 12 and references cited therein
- [4] Chung H, Weinberger M B, Levine J B, Cavner A, Yang J M, Tolbert S H and Kaner R B 2007 *Science* **316** 436
- [5] Guillermet A F and Grimvall G 1989 *Phys. Rev. B* **40** 10582
- [6] Haguland J, Grimvall G, Jalborg T and Guillermet A F 1991 *Phys. Rev. B* **43** 14400
- [7] Haguland J, Guillermet A F, Grimvall G and Korling M 1993 *Phys. Rev. B* **48** 11685
- [8] Grossman J C, Mizel A, Cote M, Cohen M L and Louie S G 1999 *Phys. Rev. B* **60** 6343
- [9] Hugosson H W, Eriksson O, Jansson U and Johansson B 2001 *Phys. Rev. B* **63** 134108

- [10] Ono S, Kikegawa T and Ohishi Y 2005 *Solid State Commun.* **133** 55
- [11] Juarez-Arellano E A, Winkler B, Frierich A, Bayarjargal L, Milman V, Yan J and Clark S M 2009 *J. Alloys Compounds* **481** 577
- [12] Young A F, Sanloup C, Gregoryanz E, Scandolo S, Hemley R J and Mao H 2006 *Phys. Rev. Lett.* **96** 15501
- [13] Friederich A, Winkler B, Bayarjargal L, Morgenorth W, Juarez-Arellano E A, Milman V, Refson K, Kunz M and Chen K 2010 *Phys. Rev. Lett.* **105** 085504
- [14] Kempton C P and Nadler M R 1960 *J. Chem. Phys.* **33** 1580
- [15] Subramanian N, Chandra Shekar N V, Sanjay Kumar N R and Sahu P Ch 2006 *Curr. Sci.* **91** 175
- [16] Heinz D L and Jeanloz R 1987 Temperature measurements in the laserheated diamond cell *High-Pressure Research in Mineral Physics* ed M H Manghnani and Y Syono (Tokyo: Terra Scientific) (Washington, DC: American Geophysical Union) pp 113–27
- [17] Decker D L 1971 *J. Appl. Phys.* **42** 3239
- [18] Wu E 1989 *J. Appl. Crystallogr.* **22** 506–10
- [19] Boer F R, Boom R, Mattens W C M, Miedema A R and Niessen A K 1988 *Cohesion in Metals* (Amsterdam: North-Holland)
- [20] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k* ed K Schwarz (Austria: Vienna University of Technology) ISBN 3-9501031-1-2
- [21] Perdew J P, Burke K and Ernzerof M 1996 *Phys. Rev. Lett.* **77** 3865
- [22] Juarez-Arellano E A, Winkler B, Freidreich A, Wilson D J, Koch-Muller M, Knorr K, Vogel S C, Wall J J, Reiche H, Crichton W, Ortega-Aviles M and Borja M A 2008 *Z. Kristallogr.* **223** 492–501
- [23] Du X P and Wang Y X 2010 *J. Appl. Phys.* **107** 053506
- [24] Paneta C, Mihut I, Ledbetter H, Betts J B, Zhao Y, Daemen L L, Cynn H and Migliori A 2009 *Acta Mater.* **57** 544–8
- [25] Simunek A and Vackar J 2006 *Phys. Rev. Lett.* **96** 085501
- [26] Simunek A 2007 *Phys. Rev. B* **75** 172108