materials

MDPI

Supplementary materials for the manuscript

Carbides and Nitrides of Zirconium and Hafnium

Sergey V. Ushakov [1,*], Alexandra Navrotsky [1,*], Qi-Jun Hong [2,*] and Axel van de Walle [2,*]

[1] Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California at Davis, Davis, CA 95616, USA
[2] School of Engineering, Brown University, Providence, RI, 02912, USA
* Correspondence: svushakov@ucdavis.edu (S.V.U.); anavrotsky@ucdavis.edu (A.N.); qhong@alumni.caltech.edu (Q.J.H.); avdw@brown.edu (A.W.)

Table S1. The selected reactions for preparation of carbides and nitrides of Zr and Hf.

Reaction	ΔH_{rxn} kJ/mol	ΔS_{rxn} J/mol/K	Note‡
Carbides preparation		Graphite reaction with metal or hydride	
Zr(s) + C (graphite)= ZrC(s)	-196	-11	
Hf(s) + C (graphite)= HfC(s)	-230	-8	
ZrH_2(s) + C (graphite)= ZrC(s) +H_2(g)	-276	123	
HfH_2(s) + C (graphite)= HfC(s) +H_2(g)	NA	NA	
		Carburizing gas reaction with metal	
Zr(s) + 2CO(g) = ZrC(s) + CO_2(g)	-317	-191	ΔG < 0 at T < 1750 °C
Hf(s) + 2CO(g) = HfC(s) + CO_2(g)	-361	-201	ΔG < 0 at T <1950 °C
		Carbothermal process	
ZrO_2(s) +3C (graphite) = ZrC(s) + 2CO(g)	680	361	ΔG < 0 at T > 1652 °C
HfO_2(s) + 3C (graphite) = HfC(s) + 2CO(g)	662	360	ΔG < 0 at T > 1642 °C
Nitrides preparation		Metals/metal hydrides nitridation	
Hf(s) + ½ N_2(g) = HfN (s)	-369	-88	
Zr(s) + ½ N_2(g) = ZrN (s)	-365	-95	
ZrH_2(s) + ½ N_2(g) = ZrN (s) +H_2(g)	-196	39	
HfH_2(s) + ½ N_2(g) = HfN (s) + H_2(g)	NA	NA	
			Carbothermal nitridation
ZrO_2(s) + 2C (graphite) + ½ N_2 = ZrN(s) + 2CO(g)	511	276	ΔG < 0 at T > 1620 °C
HfO_2(s) + 2C (graphite) + ½ N_2 = HfN(s) + 2CO(g)	523	279	ΔG < 0 at T > 1680 °C
ZrO_2(s) + 2C (graphite) + NH_3 = ZrN(s) + 2CO(g) + 1.5H_2	553	381	ΔG < 0 at T > 1180 °C
HfO_2(s) + 2C (graphite) + NH_3 = HfN(s) + 2CO(g) + 1.5H_2	569	378	ΔG < 0 at T > 1220 °C
ZrC(s) + 0.5N_2(g) = ZrN(s) + C (graphite)	-168	-85	ΔG < 0 at T < 1700 °C
HfC(s) + 0.5N_2(g) = HfN(s) + C (graphite)	-134	-80	ΔG < 0 at T < 1500 °C

†Enthalpies, entropies and free energies (ΔG) of the reactions are from FactSage 5.4 database (www.factsage.com). ‡For reactions with temperatures of the ΔG sign change not indicated, ΔG is negative for the range of stability of reactants

Table S2. Cell parameters for NaCl –type compounds reported in Hf-Zr-C-O-N system.

Formula	a, Å	ICSD	Year	Authors	Title	Reference
HfC	4.63078	159873	2008	Nakamura, K.; Yashima, M.	Crystal structure of (NaCl)-type transition metal monocarbides M C (M =V, Ti, Nb, Ta, Hf, Zr), a neutron powder diffraction study	Materials Science & Engineering, B: Advanced Functional Solid-State Materials (2008) 148, p69-p72
HfC	4.637	658398	1995	Lengauer, W.; Binder, S.; Aigner, K.; Ettmayer, P.; Guillou, A.; Debuigne, J.; Groboth, G.	Solid state properties of group IVb carbonitrides	Journal of Alloys and Compounds (1995) 217, (1) p137-p147
HfC	4.65	658336	1994	Aigner, K.; Lengauer, W.; Rafaja, D.; Ettmayer, P.	Lattice parameters and thermal expansion of $Ti(C_xN_{1-x})$, $Zr(C_xN_{1-x})$, $Hf(C_xN_{1-x})$ and TiN_{1-x} from 298 to 1473 K as investigated by high-temperature X-ray diffraction	Journal of Alloys and Compounds (1994) 215, (1) p121-p126
HfC	4.633	618016	1984	Valvoda, V.	X-ray Debye temperatures of HfC and alpha-W_2C	Physica Status Solidi A: Applied Research (1984) 83, (2) p123-125
HfC	4.64	618010	1977	Rogl, Peter; Naik, Subhash K.; Rudy, Erwin	A constitutional diagram of the system TiC - HfC - WC	Monatshefte fuer Chemie (1977) 108, (5) p1189-p1211
HfC	4.635	618013	1977	Dubrovskaya, L.B.; Zaytsev, G.P.; Ordanyan, S.S.	Magnetic susceptibility of solid solutions of hafnium and tantalum monocarbides	Physics of Metals and Metallography (1977) 44, (6) p173-p177
HfC	4.623	618008	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'Hf O' - HfN - HfC	Monatshefte fuer Chemie (1975) 106, (4) p973-p981
HfC	4.623	618009	1975	Gatterer, J.; Dufek, G.; Ettmayer, P.; Kieffer, R.	Das kubische Tantalmononitrid (B1-Typ) und seine Mischbarkeit mit den isotypen Uebergangsmetallnitriden und-carbiden	Monatshefte fuer Chemie (1975) 106, (5) p1137-p1147
HfC	4.674	618017	1975	Achour, M.; Zaug, J.; Pialoux, A.	Etude de la carboreduction progressive du dioxyde de hafnium. III. - Determination du parametre cristallin de la phase HfC limite puis sous vide par diffraction des rayons X entre 1000 C et 2000 C	Revue Internationale des Hautes Temperatures et des Refractaires (1975) 12, (3) p289-p294
HfC	4.623	618011	1972	Kieffer, R.; Nowotny, H.; Ettmayer, P.; Dufek, G.	Neue Untersuchungen ueber die Mischbarkeit von Uebergangsmetallnitriden und -karbiden	Metall (Clausthal-Zellerfeld, Germany) (1972) 26, (7) p701-p708
HfC	4.64	617998	1968	Ramqvist, Lars	Variation of lattice parameter and hardness with carbon content of group 4b metal carbides	Jernkontorets Annaler (1968) 152, p 517-523
HfC	4.631	618002	1968	Pessall, N.; Gold, R.E.; Johansen, H.A.	A study of superconductivity in interstitial compounds	Journal of Physics and Chemistry of Solids (1968) 29, (1) p19-p38

Formula	a, Å	ICSD	Year	Authors	Title	Reference
HfC	4.65	618018	1967	Denbnovetskaya, E.N.	Preparation of solid solutions of some complex carbides of the transition metals	Soviet Powder Metallurgy and Metal Ceramics (1967) 6, (3) p194-p197
HfC	4.643	618020	1965	Sara, R.V.	The hafnium-carbon system	Transactions of the Metallurgical Society of AIME (1965) 233, p1683-p1691
HfC	4.64	198351	1963	Krikorian, N.H.; Witteman, W.G.; Bowman, M.G.	The mutual solid solubility of hafnium carbide and uranium monocarbide	Journal of the Electrochemical Society (1963) 110, (6) p560-p563
HfC	4.6395	618000	1963	Krikorian, N.H.; Wallace, T.C.; Anderson, James L.	Low-temperature thermal expansion of the group 4a carbides	Journal of the Electrochemical Society (1963) 110, (6) p587-p588
HfC	4.632	618005	1963	Rudy, E.; Benesovsky, F.	Zur Kenntnis der Stabilitaet des Urandicarbids und der Kohlenstoff-stabilen Bereiche in den Partialsystemen von UC mit ZrC, HfC, NbC und TaC	Monatshefte fuer Chemie (1963) 94, (1) p204-p224
HfC	4.628	618015	1961	Nowotny, H.; Laube, E.	Die thermische Ausdehnung hochschmelzender Phasen	Planseeberichte fuer Pulvermetallurgie (1961) 9, p54-p59
HfC	4.628	108134	1960	Benesovsky, F.; Rudy, E.	Beitrag zum Aufbau des Systeme Zirkonium-Kohlenstoff und Hafnium-Kohlenstoff	Planseeberichte fuer Pulvermetallurgie (1960) 8, p66-p71
HfC	4.63	618004	1960	Nowotny, H.; Benesovsky, F.; Rudy, E.	Hochschmelzende Systeme mit Hafniumkarbid und -nitrid	Monatshefte fuer Chemie (1960) 91, (2) p348-p356
HfC	4.64	618003	1959	Nowotny, H.; Kieffer, R.; Benesovsky, F.; Brukl, C.	Ueber die Teilsysteme: TiC - HfC und ZrC - HfC	Monatshefte fuer Chemie (1959) 90, (1) p86-p88
HfC	4.641	22262	1954	Cotter, P.G.; Kohn, J.A.	Industrial diamond substitutes: I. Physical and x-ray study of hafnium carbide.	Journal of the American Ceramic Society (1954) 37, p415-p420
HfC	4.64	618001	1953	Glaser, Frank W.; Moskowitz, David; Post, Benjamin	A study of some binary hafnium compounds	Journal of Metals (1953) 5, p1119-p1120
HfC_{1-x}						
$HfC_{0.901}$	4.638	43371	1962	Bittner, H.; Goretzki, H.	Magnetische Untersuchungen der Carbide TiC, ZrC, HfC, VC, Nb C und TaC	Monatshefte fuer Chemie (1962) 93, p1000-p1004
$HfC_{0.95}$	4.648	618007	1971	Samsonow, G.W.; Morosow, W.W.	Carbohydride der Uebergangsmetalle	Monatshefte fuer Chemie (1971) 102, (6) p1667-p1678
$HfC_{0.96}$	4.6393	617997	1970	Samsonov, G.V.; Timofeeva, I.I.	X-ray diffraction study of dynamic characteristics of crystal lattices of some interstitial phases	Dopovidi Akademii Nauk Ukrains'koi RSR, Seriya A: Fiziko-Tekhnichni ta Matematichni Nauki (1970) 1970, (9) p831-p833

Formula	a, Å	ICSD	Year	Authors	Title	Reference
$HfC_{0.71}$	4.627		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides.	Metallurgiya: 1991; p 352 (in Russian)
$HfC_{0.85}$	4.637					
$HfC_{0.99}$	4.642					
$HfC_{0.97}$	4.6424		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.96}$	4.6422					
$HfC_{0.95}$	4.6420					
$HfC_{0.94}$	4.6418					
$HfC_{0.93}$	4.6416					
$HfC_{0.92}$	4.6414					
$HfC_{0.91}$	4.6411		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.90}$	4.6408					
$HfC_{0.89}$	4.6405					
$HfC_{0.88}$	4.6401					
$HfC_{0.87}$	4.6397					
$HfC_{0.86}$	4.6393					
$HfC_{0.85}$	4.6389		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.84}$	4.6385					
$HfC_{0.83}$	4.6380					
$HfC_{0.82}$	4.6376					
$HfC_{0.81}$	4.6372					
$HfC_{0.80}$	4.6377					
$HfC_{0.79}$	4.6363		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.78}$	4.6358					
$HfC_{0.77}$	4.6354					
$HfC_{0.76}$	4.6348					
$HfC_{0.75}$	4.6344					
$HfC_{0.74}$	4.6338					
$HfC_{0.73}$	4.6334		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.72}$	4.6328					
$HfC_{0.71}$	4.6324					
$HfC_{0.70}$	4.6318					
$HfC_{0.69}$	4.6313					
$HfC_{0.68}$	4.6307		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.67}$	4.6301					
$HfC_{0.66}$	4.6295					

Formula	a, Å	ICSD	Year	Authors	Title	Reference
$HfC_{0.65}$	4.6290					
$HfC_{0.64}$	4.6284					
$HfC_{0.63}$	4.6278					
$HfC_{0.62}$	4.6271		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.61}$	4.6265					
$HfC_{0.60}$	4.6258					
$HfC_{0.59}$	4.6251					
$HfC_{0.58}$	4.6244					
$HfC_{0.57}$	4.6237					
$HfC_{0.56}$	4.6229					
$HfC_{0.55}$	4.6221		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$HfC_{0.54}$	4.6214					
$HfC_{0.53}$	4.6205					
$HfC_{0.52}$	4.6196					
$HfC_{0.51}$	4.6188					
$HfC_{0.84}O_{0.16}$	4.618	196637	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'HfO' - HfN - HfC	Monatshefte fuer Chemie (1975) 106, (4) p973-p981
$HfC_{0.39}O_{0.61}$	4.603	196638				
$HfC_{0.923}O_{0.058}$	4.638		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides.	Metallurgiya: 1991; p 352 (in Russian)
Hf-C-N						
$HfC_{0.5}N_{0.5}$	4.572	77009	1960	Nowotny, H.N.; Benesovsky, F.; Rudy, E.	Hochschmelzende Systeme mit Hafniumkarbid und -nitrid	Monatshefte fuer Chemie (1960) 91, p348-p356
$HfC_{0.25}N_{0.75}$	4.538					
$HfC_{0.5}N_{0.5}$	4.569	618025	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'HfO' - HfN - HfC	Monatshefte fuer Chemie (1975) 106, (4) p973-p980
$HfC_{0.75}N_{0.25}$	4.597					
$HC_{0.5}N_{0.5}$	4.573	618026	1972	Kieffer, R.; Nowotny, H.; Ettmayer, P.; Dufek, G.	Neue Untersuchungen ueber die Mischbarkeit von Uebergangsmetallnitriden und -karbiden	Metall (Clausthal-Zellerfeld, Germany) (1972) 26, (7) p701-p708
$HfC_{0.5}N_{0.5}$	4.6	658337	1994	Aigner, K.; Lengauer, W.; Rafaja, D.; Ettmayer, P.	Lattice parameters and thermal expansion of $Ti(C_xN_{1-x})$, $Zr(C_xN_{1-x})$, $Hf(C_xN_{1-x})$ and TiN_{1-x} from 298 to 1473 K as investigated by high-temperature X-ray diffraction	Journal of Alloys and Compounds (1994) 215, (1) p121-p126
$HfC_{0.5}N_{0.5}$	4.583	658399	1995	Lengauer, W.; Binder, S.; Aigner, K.; Ettmayer, P.; Guillou, A.; Debuigne, J.; Groboth, G.	Solid state properties of group IVb carbonitrides	Journal of Alloys and Compounds (1995) 217, (1) p137-p147

Formula	a, Å	ICSD	Year	Authors	Title	Reference
$HfC_{0.820}N_{0.163}$	4.623		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides.	Metallurgiya: 1991; p 352 (in Russian)
$HfC_{0.540}N_{0.434}$	4.584					
$HfC_{0.291}N_{0.664}$	4.550					
Hf-N-O						
$HfN_{0.92}O_{0.08}$	4.523		1975	Constant, K Kieffer, R. Ettmayer, P	Ueber das pseudoternaere System 'HfO' - HfN - HfC	Monatshefte fuer Chemie (1975) 106, (4) p973-p980
$HfN_{0.85}O_{0.15}$	4.524	196635				
$HfN_{0.8}O_{0.2}$	4.524					
$HfN_{0.75}O_{0.25}$	4.525					
$HfN_{0.70}O_{0.30}$	4.523					
$HfN_{0.60}O_{0.40}$	4.526					
$HfN_{0.40}O_{0.60}$	4.534	196636				
$HfN_{0.80}O_{0.09}$	4.534		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides.	Metallurgiya: 1991; p 352 (in Russian)
HfN						
HfN	4.526	658397	1995	Lengauer, W.; Binder, S.; Aigner, K.; Ettmayer, P.; Guillou, A.; Debuigne, J.; Groboth, G.	Solid state properties of group IVb carbonitrides	Journal of Alloys and Compounds (1995) 217, (1) p137-p147
HfN	4.55	658335	1994	Aigner, K.; Lengauer, W.; Rafaja, D.; Ettmayer, P.	Lattice parameters and thermal expansion of $Ti(C_xN_{1-x})$, $Zr(C_xN_{1-x})$, $Hf(C_xN_{1-x})$ and TiN_{1-x} from 298 to 1473 K as investigated by high-temperature X-ray diffraction	Journal of Alloys and Compounds (1994) 215, (1) p121-p126
$HfN_{0.95}$	4.526		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides.	Metallurgiya: 1991; p 352 (in Russian)
$HfN_{1.09}$	4.510					
HfN	4.516	638655	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'HfO' - HfN - HfC	Monatshefte fuer Chemie (1975) 106, (4) p973-p981
HfN	4.517	638656	1975	Gatterer, J.; Dufek, G.; Ettmayer, P.; Kieffer, R.	Das kubische Tantalmononitrid (B1-Typ) und seine Mischbarkeit mit den isotypen Uebergangsmetallnitriden und-carbiden	Monatshefte fuer Chemie (1975) 106, (5) p1137-p1147
HfN	4.5101	53026	1972	Timofeeva, I.I.; Shvedova, L.K.	Microhardness and thermal expansion of transition metal nitrides at 80-300 K	Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy (1972) 8, p1169-p1170
HfN	4.516	638660	1972	Kieffer, R.; Nowotny, H.; Ettmayer, P.; Dufek, G.	Neue Untersuchungen ueber die Mischbarkeit von Uebergangsmetallnitriden und –karbiden	Metall (Clausthal-Zellerfeld, Germany) (1972) 26, (7) p701-p708

Formula	a, Å	ICSD	Year	Authors	Title	Reference
HfN	4.526	196611	1971	Kieffer, R.; Ettmayer, P.; Petter, F.	Beitrag zur Kenntnis der Systeme Titan -Chrom -Stickstoff, Zirkonium - Chrom - Stickstoff und Hafnium - Chrom – Stickstoff	Monatshefte fuer Chemie (1971) 102, (5) p1182-p1196
HfN	4.518	638657	1970	Rudy, Erwin	The crystal structures of Hf_3N_2 and Hf_4N_3	Metallurgical and Materials Transactions B: Processing Science (1970) 1, (5) p1249-p1252
HfN	4.512	638650	1968	Pessall, N.; Gold, R.E.; Johansen, H.A.	A study of superconductivity in interstitial compounds	Journal of Physics and Chemistry of Solids (1968) 29, (1) p19-p38
HfN	4.52	638654	1968	Holleck, H.; Smailos, E.; Thuemmler, F.	Zur Mischkristallbildung in den quasibinaeren Systemen von UN und den Mononitriden der IV A-Gruppe Ti N, Zr N und Hf N	Monatshefte fuer Chemie (1968) 99, (3) p985-p989
HfN	4.512	638649	1967	Yen, C.M.; Toth, L.E.; Shy, Y.M.; Anderson, D.E.; Rosner, L.G.	Superconducting Hc-Jc and Tc measurements in the Nb-Ni-N, Nb-Hf-N, and Nb-V-N ternary systems	Journal of Applied Physics (Melville, NY, United States) (1967) 38, (5) p2268-p2271
HfN	4.518	638652	1961	Rudy, E.; Benesovsky, F.	Untersuchungen in den Systemen: Hafnium - Bor - Stickstoff und Zirkonium - Bor - Stickstoff	Monatshefte fuer Chemie (1961) 92, (2) p415-p441
HfN	4.52	638651	1960	Nowotny, H.; Benesovsky, F.; Rudy, E.	Hochschmelzende Systeme mit Hafniumkarbid und -nitrid	Monatshefte fuer Chemie (1960) 91, (2) p348-p356
HfN	4.52	76129	1953	Glaser, Frank W.; Moskowitz, David; Post, Benjamin	A study of some binary hafnium compounds	Journal of Metals (1953) 5, p1119-p1120
HfN	4.682	53025	1971	Zainulin, Yu.G.; Alyamovskii, S.I.; Shveikin, G.P.; Gel'd, P.V.	Coefficients of thermal expansion of cubic (NaCl-type) oxycarbides and oxynitrides of zirconium and hafnium	Tepolfizika Vysokikh Temperatur (1971) 9, p496-p499
ZrC						
ZrC	4.694	619157	1950	Duwez, Pol; Odell, Francis	Phase relationships in the binary systems of nitrides and carbides of zirconium, columbium, titanium, and vanadium	Journal of the Electrochemical Society (1950) 97, (10) p299-p304
ZrC	4.683	44730	1956	Samsonov, G.V.; Rozinova, N.S.	Some physicochemical propertierties of alloys of zirconium with carbon	Izvestiya Sektora Platiny i Drugikh Blagorodnykh Metallov, Institut Obshchei i Neorganicheskoi Khimii, Akademiya Nauk SSSR (1956) 27, (*) p126-p132
ZrC	4.689	619179	1956	Tombrel, F.	Contribution a l'etude du systeme ternaire C Ti - C Zr - C W	Plansee Proceedings, Papers Presented at the Plansee Seminar, "De Re Metallica", 1955, 2nd (1956) 1956, (*) p205-p215

Formula	a, Å	ICSD	Year	Authors	Title	Reference
ZrC	4.6828	44495	1958	Elliott, R.O.; Kempter, C.P.	Thermal expansion of some transition metal carbides	Journal of Chemical Physics (1958) 62, (*) p630-p631
ZrC	4.696	619159	1959	Brownlee, L.D.	The pseudo-binary systems of uranium carbide with zirconium carbide, tantalum carbide, and niobium carbide	Journal of the Institute of Metals (1959) 87, (*) p58-p61
ZrC	4.694	619172	1960	Benesovsky, F.; Rudy, E.	Beitrag zum Aufbau des Systeme Zirkonium-Kohlenstoff und Hafnium-Kohlenstoff	Planseeberichte fuer Pulvermetallurgie (1960) 8, (*) p66-p71
ZrC	4.687	619151	1963	Smith, Deane K.; Cline, Carl F.	An X-ray investigation of polymorphism in ZrC	Journal of the American Ceramic Society (1963) 46, (11) p566-p566
ZrC	4.6986	619158	1963	Krikorian, N.H.; Wallace, T.C.; Anderson, James L.	Low-temperature thermal expansion of the group 4a carbides	Journal of the Electrochemical Society (1963) 110, (6) p587-p588
ZrC	4.696	619166	1963	Rudy, E.; Benesovsky, F.	Zur Kenntnis der Stabilitaet des Urandicarbids und der Kohlenstoff-stabilen Bereiche in den Partialsystemen von U C mit Zr C, Hf C, Nb C und Ta C	Monatshefte fuer Chemie (1963) 94, (1) p204-p224
ZrC	4.694	619178	1963	Ivanov, O.S.; Alekseeva, Z.M.	Investigation of the structure of alloys of the systems U C - Zr C, U C - Th C, AND Th C - Zr C	Stroenie Splavov Nekotorykh Sistem s Uranom i Toriem (1963) 1963, (*) p419-p429
ZrC	4.6983	619152	1965	Sara, R.V.	The system zirconium-carbon	Journal of the American Ceramic Society (1965) 48, (5) p243-p247
ZrC	4.682	619153	1966	Avgustinik, A.I.; Ordan''yan, S.S.	Structure of alloys in the system Zr-C-Ta	Journal of Applied Chemistry of the USSR (1966) 39, (2) p289-p293
ZrC	4.68	619173	1967	Denbnovetskaya, E.N.	Preparation of solid solutions of some complex carbides of the transition metals	Soviet Powder Metallurgy and Metal Ceramics (1967) 6, (3) p194-p197
ZrC	4.697	619156	1968	Ramqvist, Lars	Variation of lattice parameter and hardness with carbon content of group 4b metal carbides	Jernkontorets Annaler (1968) 152, (*) p517-p523
ZrC	4.69	619162	1968	Pessall, N.; Gold, R.E.; Johansen, H.A.	A study of superconductivity in interstitial compounds	Journal of Physics and Chemistry of Solids (1968) 29, (1) p19-p38
ZrC	4.6983	619177	1968	Nickel, Hubertus; Inanc, Oezel; Luecke, Kurt	Beitrag zum System Zirkonium-Kohlenstoff	Zeitschrift fuer Metallkunde (1968) 59, (12) p935-p940
ZrC	4.693	619160	1970	Stuart, H.; Ridley, N.	Thermal expansions of some carbides and tessellated stresses in steel	Journal of the Iron and Steel Institute, London (1970) 208, (*) p1087-p1092
ZrC	4.694	619171	1972	Kieffer, R.; Nowotny, H.; Ettmayer, P.; Dufek, G.	Neue Untersuchungen ueber die Mischbarkeit von Uebergangsmetallnitriden und -karbiden	Metall (Clausthal-Zellerfeld, Germany) (1972) 26, (7) p701-p708

Formula	a, Å	ICSD	Year	Authors	Title	Reference
ZrC	4.697	619148	1975	Bukatov, V.G.; Knyazev, V.I.; Korostin, O.S.; Baranov, V.M.	Temperature dependence of the Young's modulus of metalline carbides	Inorganic Materials (1975) 11, (2) p310-p312
ZrC	4.694	619169	1975	Gatterer, J.; Dufek, G.; Ettmayer, P.; Kieffer, R.	Das kubische Tantalmononitrid (B1-Typ) und seine Mischbarkeit mit den isotypen Uebergangsmetallnitriden und-carbiden	Monatshefte fuer Chemie (1975) 106, (5) p1137-p1147
ZrC	4.699	619170	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'ZrO' - ZrN - ZrC	Monatshefte fuer Chemie (1975) 106, (4) p823-p832
ZrC	4.692	619174	1977	Funke, V.F.; Pshenichnyi, I.V.; Zubarev, P.V.; Pliner, L.A.; Lyakhov, D.M.; Golomazov, V.M.	Some physicomechanical properties of Zr C - Nb C - Mo C1-x alloys	Soviet Powder Metallurgy and Metal Ceramics (1977) 16, (12) p968-p973
ZrC	4.697	619155	1978	Benedict, U.; Richter, K.; Walker, C.T.	Solubility study in the systems PuC-ZrC and PuC-TaC	Journal of the Less-Common Metals (1978) 60, (1) p123-p133
ZrC	4.699	619149	1979	Lesnaya, M.I.; Nemchenko, V.F.; Savin, V.I.	Some properties of solid solutions TiC - ZrC	Inorganic Materials (1979) 15, (1) p61-p64
ZrC	4.71	619147	1981	Matsumoto, Osamu; Yaguchi, Yoichi; Kajiwara, Toshio; Konuma, Mitsuharu; Kanzaki, Yasushi	Preparation and properties of a cubic solid solution in the Mo-Zr-C system	High Temperature Science (1981) 14, (*) p161-p169
ZrC	4.6896	600759	1984	Rahimzadeh, Ebrahim; Joshi, Narayan R.; Singh, Sohan	Thermal expansion of ZrC from 120 to 300 K by an X-ray powder method	Journal of the American Ceramic Society (1984) 67, (7) pC-139-pC-140
ZrC	4.7	619150	1987	Kosukhin, V.V.; Funke, V.F.; Minashkin, V.I.; Smirnov, V.S.; Efremov, Yu.P.	Zirconium nitride and carbonitride coatings obtained by the chemical vapor deposition (CVD) method	Inorganic Materials (1987) 23, (1) p52-p56
ZrC	4.692	658395	1995	Lengauer, W.; Binder, S.; Aigner, K.; Ettmayer, P.; Guillou, A.; Debuigne, J.; Groboth, G.	Solid state properties of group IVb carbonitrides	Journal of Alloys and Compounds (1995) 217, (1) p137-p147
ZrC	4.69106	159874	2008	Nakamura, K.; Yashima, M.	Crystal structure of (NaCl)-type transition metal monocarbides MC (M =V, Ti, Nb, Ta, Hf, Zr), a neutron powder diffraction study	Materials Science & Engineering, B: Advanced Functional Solid-State Materials (2008) 148, (*) p69-p72

Formula	a, Å	ICSD	Year	Authors	Title	Reference
ZrC_{1-x}						
$ZrC_{0.85}$	4.692	619168	1971	Samsonow, G.W.; Morosow, W.W.	Carbohydride der Uebergangsmetalle	Monatshefte fuer Chemie (1971) 102, (6) p1667-p1678
$ZrC_{0.9}$	4.6929	77575	1970	Samsonov, G.V.; Timofeeva, I.I.	X-ray diffraction study of dynamic characteristics of crystal lattices of some interstitial phases	Dopovidi Akademii Nauk Ukrains'koi RSR, Seriya A: Fiziko-Tekhnichni ta Matematichni Nauki (1970) 1970, (9) p831-p833
$ZrC_{0.9}$	4.698	57069	1990	Christensen, A.N.	A neutron diffraction investigation on single crystals of titanium oxide, zirconium carbide and hafnium nitride	Acta Chemica Scandinavica (1990) 44, (*) p851-p852
$ZrC_{0.92}$	4.689	619154	1968	Vil''k, Yu.N.; Danisina, I.N.; Omel''chenko, Y.A.; Ryzhkova, T.P.	Variations of certain physicochemical properties in the system zirconium carbide - zirconium nitride	Journal of Applied Chemistry of the USSR (1968) 41, (4) p873-p875
$ZrC_{0.957}$	4.691	43370	1962	Bittner, H.; Goretzki, H.	Magnetische Untersuchungen der Carbide TiC, ZrC, HfC, VC, NbC und TaC	Monatshefte fuer Chemie (1962) 93, (*) p1000-p1004
$Zr_{0.35}C_{0.65}$	4.698	292096	1965	Sara, R.V.	The system zirconium-carbon	Journal of the American Ceramic Society (1965) 48, (5) p243-p247
$Zr_{0.615}C_{0.385}$	4.6941	292095				
$ZrC_{0.69}$	4.689		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides. (Table 20 p 95)	Metallurgiya: 1991; p 352 (in Russian)
$ZrC_{0.76}$	4.697					
$ZrC_{0.99}$	4.698					
$ZrC_{0.97}$	4.6975		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$ZrC_{0.96}$	4.6981					
$ZrC_{0.95}$	4.6986					
$ZrC_{0.94}$	4.6991					
$ZrC_{0.93}$	4.6996					
$ZrC_{0.92}$	4.7000					
$ZrC_{0.91}$	4.7004		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$ZrC_{0.90}$	4.7007					
$ZrC_{0.89}$	4.7011					
$ZrC_{0.88}$	4.7013					
$ZrC_{0.87}$	4.7016					
$ZrC_{0.86}$	4.7018					
$ZrC_{0.85}$	4.7019					
$ZrC_{0.84}$	4.7020					

Formula	a, Å	ICSD	Year	Authors	Title	Reference
$ZrC_{0.83}$	4.7021					
$ZrC_{0.82}$	4.7021					
$ZrC_{0.81}$	4.7021					
$ZrC_{0.80}$	4.7020		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$ZrC_{0.79}$	4.7019					
$ZrC_{0.78}$	4.7018					
$ZrC_{0.77}$	4.7017					
$ZrC_{0.76}$	4.7016					
$ZrC_{0.75}$	4.7014					
$ZrC_{0.74}$	4.7012					
$ZrC_{0.73}$	4.7010		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$ZrC_{0.72}$	4.7008					
$ZrC_{0.71}$	4.7006					
$ZrC_{0.70}$	4.7003					
$ZrC_{0.69}$	4.7000					
$ZrC_{0.68}$	4.6996					
$ZrC_{0.67}$	4.6993					
$ZrC_{0.66}$	4.6988		1974	G. V. Samsonov, G. S. Upadhyaya, and V. S. Neshpor	Physical Materials Science of Carbides (in Russian)	Naukova Dumka Kiev, (1974).
$ZrC_{0.65}$	4.6983					
$ZrC_{0.64}$	4.6976					
$ZrC_{0.63}$	4.6965					
$ZrC_{0.62}$	4.6950					
Zr-C-N						
$ZrC_{0.5}N_{0.5}$	4.635	77213	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System ZrO-ZrN-ZrC	Monatshefte fuer Chemie (1975) 106, (*) p823-p832
$ZrN_{0.52}C_{0.48}$	4.632	196652				
$ZrC_{0.5}N_{0.5}$	4.635	618441	1987	Kosukhin, V.V.; Funke, V.F.; Minashkin, V.I.; Smirnov, V.S.; Efremov, Yu.P.	Zirconium nitride and carbonitride coatings obtained by the chemical vapor deposition (CVD) method	Inorganic Materials (1987) 23, (1) p52-p56
$Zr_2C_{0.92}N_{0.82}$	4.642	618442	1968	Vil''k, Yu.N.; Danisina, I.N.; Omel''chenko, Y.A.; Ryzhkova, T.P.	Variations of certain physicochemical properties in the system zirconium carbide - zirconium nitride	Journal of Applied Chemistry of the USSR (1968) 41, (4) p873-p875
$ZrC_{0.5}N_{0.5}$	4.638	618445	1972	Kieffer, R.; Nowotny, H.; Ettmayer, P.; Dufek, G.	Neue Untersuchungen ueber die Mischbarkeit von Uebergangsmetallnitriden und -karbiden	Metall (Clausthal-Zellerfeld, Germany) (1972) 26, (7) p701-p708

Formula	a, Å	ICSD	Year	Authors	Title	Reference
$ZrC_{0.5}N_{0.5}$	4.66	658334	1994	Aigner, K.; Lengauer, W.; Rafaja, D.; Ettmayer, P.	Lattice parameters and thermal expansion of $Ti(C_xN_{1-x})$, $Zr(C_xN_{1-x})$, $Hf(C_xN_{1-x})$ and TiN_{1-x} from 298 to 1473 K as investigated by high-temperature X-ray diffraction	Journal of Alloys and Compounds (1994) 215, (1) p121-p126
$ZrC_{0.5}N_{0.5}$	4.636	658396	1995	Lengauer, W.; Binder, S.; Aigner, K. et al.	Solid state properties of group IVb carbonitrides	Journal of Alloys and Compounds (1995) 217, (1) p137-p147
$ZrC_{0.78}N_{0.18}$	4.680		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides. (Table 81 p. 194)	Metallurgiya: 1991; p 352 (in Russian)
$ZrC_{0.62}N_{0.36}$	4.668					
$ZrC_{0.37}N_{0.63}$	4.625					
Zr-C-O						
$ZrC_{0.71}O_{0.29}$	4.667	196655	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'ZrO' - ZrN - ZrC	Monatshefte fuer Chemie (1975) 106, (4) p823-p832
$ZrC_{0.31}O_{0.69}$	4.643	196656				
$ZrC_{0.96}O_{0.04}$	4.698	181839	2011	Gendre, M.; Maitre, A.; Trolliard, G.	Synthesis of zirconum oxycarbide (ZrC_xO_y) powders: influence of stoichiometry on densification kinetics during spark plasma sintering and on mechanical properties	Journal of the European Ceramic Society (2011) 31, (13) p2377-p2385
$ZrC_{0.94}O_{0.05}$	4.695	181840				
$ZrC_{0.89}O_{0.07}$	4.688	181841				
$ZrC_{0.79}O_{0.13}$	4.68	181842				
ZrN						
ZrN	4.585	41934	1975	Christensen, A.N.	A neutron diffraction investigation of single crystals of titanium carbide, titanium nitride, and zirconium nitride.	Acta Chemica Scandinavica, Series A: Physical and Inorganic Chemistry (1975) 29, (*) p563-p568
ZrN	4.63	26950	1925	Becker, K.; Ebert, F.	Die Kristallstrukturen einiger binaerer Carbide und Nitride.	Zeitschrift fuer Physik (1925) 31, (*) p268-p272
ZrN	4.5745	44506	1958	Baker, T.W.	The coefficient of thermal expansion of zirconium nitride	Acta Crystallographica (1958) 11, (*) p300-p300
ZrN	4.5773	76530	1972	Timofeeva, I.I.; Shvedova, L.K.	Microhardness and thermal expansion of transition metal nitrides at 80-300 K	Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy (1972) 8, (*) p1027-p1029
ZrN	4.5783	169453	2011	Yang Xiao; Takeichi, N.; Shida, K.; Tanaka, H.; Kuriyama, N.; Sakai, T.	Novel Mg-Zr-A-H (A=Li, Na) hydrides synthesized by a high pressure technique and their hydrogen storage properties	Journal of Alloys and Compounds (2011) 509, (*) p1211-p1216
ZrN	4.68	180847	2011	Larijani, M.M.; Kiani, M.; Tanhayi, M.; Majdabadi, A.	Characterization of ion beam sputtered ZrN coatings prepared at different substrate temperatures	Crystal Research and Technology (2011) 46, (4) p351-p356
ZrN	4.65	180848				
ZrN	4.66	180849				
ZrN	4.63	180850				

Formula	a, Å	ICSD	Year	Authors	Title	Reference
ZrN	4.62	197016	1987	Kosukhin, V.V.; Funke, V.F.; Minashkin, V.I.; Smirnov, V.S.; Efremov, Yu.P.	Zirconium nitride and carbonitride coatings obtained by the chemical vapor deposition (CVD) method	Inorganic Materials (1987) 23, (1) p52-p56
ZrN	4.537	644881	1954	Schoenberg, N.	The structure of the metallic quaternary phase ZrTaNO	Acta Chemica Scandinavica (1954) 8, (*) p627-p629
ZrN	4.576	644884	1974	Gusev, A.I.; Shveikin, G.P.	Solid solutions in the system ZrN-NbC	Inorganic Materials (1974) 10, (7) p1087-p1089
ZrN	4.576	644885	1987	Kosukhin, V.V.; Funke, V.F.; Minashkin, V.I.; Smirnov, V.S.; Efremov, Yu.P.	Zirconium nitride and carbonitride coatings obtained by the chemical vapor deposition (CVD) method	Inorganic Materials (1987) 23, (1) p52-p56
ZrN	4.576	644887	1950	Duwez, Pol; Odell, Francis	Phase relationships in the binary systems of nitrides and carbides of zirconium, columbium, titanium, and vanadium	Journal of the Electrochemical Society (1950) 97, (10) p299-p304
ZrN	4.573	644888	1968	Pessall, N.; Gold, R.E.; Johansen, H.A.	A study of superconductivity in interstitial compounds	Journal of Physics and Chemistry of Solids (1968) 29, (1) p19-p38
ZrN	4.58	644889	1960	Nowotny, H.; Benesovsky, F.; Rudy, E.	Hochschmelzende Systeme mit Hafniumkarbid und -nitrid	Monatshefte fuer Chemie (1960) 91, (2) p348-p356
ZrN	4.577	644891	1961	Rudy, E.; Benesovsky, F.	Untersuchungen in den Systemen: Hafnium - Bor - Stickstoff und Zirkonium - Bor - Stickstoff	Monatshefte fuer Chemie (1961) 92, (2) p415-p441
ZrN	4.558	644892	1963	Bittner, H.; Goretzki, H.; Benesovsky, F.; Nowotny, H.	Ueber einige Monocarbid-Mononitrid-Systeme und deren magnetische Eigenschaften	Monatshefte fuer Chemie (1963) 94, (3) p518-p526
ZrN	4.577	644893	1968	Holleck, H.; Smailos, E.; Thuemmler, F.	Zur Mischkristallbildung in den quasibinaeren Systemen von UN und den Mononitriden der IV A-Gruppe Ti N, Zr N und HfN	Monatshefte fuer Chemie (1968) 99, (3) p985-p989
ZrN	4.568	644894	1971	Kieffer, R.; Ettmayer, P.; Petter, F.	Beitrag zur Kenntnis der Systeme Titan -Chrom -Stickstoff, Zirkonium - Chrom - Stickstoff und Hafnium - Chrom - Stickstoff	Monatshefte fuer Chemie (1971) 102, (5) p1182-p1196
ZrN	4.571	644895	1975	Constant, K.; Kieffer, R.; Ettmayer, P.	Ueber das pseudoternaere System 'ZrO' - ZrN - ZrC	Monatshefte fuer Chemie (1975) 106, (4) p823-p832
ZrN	4.578	644896	1975	Gatterer, J.; Dufek, G.; Ettmayer, P.; Kieffer, R.	Das kubische Tantalmononitrid (B1-Typ) und seine Mischbarkeit mit den isotypen Uebergangsmetallnitriden und-carbiden	Monatshefte fuer Chemie (1975) 106, (5) p1137-p1147

Formula	a, Å	ICSD	Year	Authors	Title	Reference
ZrN	4.571	644897	1972	Kieffer, R.; Nowotny, H.; Ettmayer, P.; Dufek, G.	Neue Untersuchungen ueber die Mischbarkeit von Uebergangsmetallnitriden und -karbiden	Metall (Clausthal-Zellerfeld, Germany) (1972) 26, (7) p701-p708
ZrN	4.6	658332	1994	Aigner, K.; Lengauer, W.; Rafaja, D.; Ettmayer, P.	Lattice parameters and thermal expansion of $Ti(C_xN_{1-x})$, $Zr(C_xN_{1-x})$, $Hf(C_xN_{1-x})$ and TiN_{1-x} from 298 to 1473 K as investigated by high-temperature X-ray diffraction	Journal of Alloys and Compounds (1994) 215, (1) p121-p126
ZrN	4.575	658394	1995	Lengauer, W.; Binder, S.; Aigner, K.; Ettmayer, P.; Guillou, A.; Debuigne, J.; Groboth, G.	Solid state properties of group IVb carbonitrides	Journal of Alloys and Compounds (1995) 217, (1) p137-p147
ZrN_{1-x}						
$ZrN_{0.82}$	4.579	644886	1968	Vil''k, Yu.N.; Danisina, I.N.; Omel''chenko, Y.A.; Ryzhkova, T.P.	Variations of certain physicochemical properties in the system zirconium carbide - zirconium nitride	Journal of Applied Chemistry of the USSR (1968) 41, (4) p873-p875
$ZrN_{0.92}$	4.575	644898	1985	Turchanin, A.G.; Babaenko, S.A.; Gusev, A.I.; Marunya, M.S.	Thermodynamic properties of complex carbide nitrides in the quasi-binary ZrN-NbC system at 298-1500 K	Russian Journal of Physical Chemistry (1985) 59, (8) p1136-p1137
$ZrN_{0.99}$	4.573	644882	1970	Samsonov, G.V.; Timofeeva, I.I.	X-ray diffraction study of dynamic characteristics of crystal lattices of some interstitial phases	Dopovidi Akademii Nauk Ukrains'koi RSR, Seriya A: Fiziko-Tekhnichni ta Matematichni Nauki (1970) 1970, (9) p831-p833
$ZrN_{0.72}$	4.577		1991	Turchanin, A. G.; Turchanin, M. A.,	Thermodynamics of Refractory Carbides and Carbonitrides.	Metallurgiya: 1991; p 352 (in Russian)
$ZrN_{0.96}$	4.570					

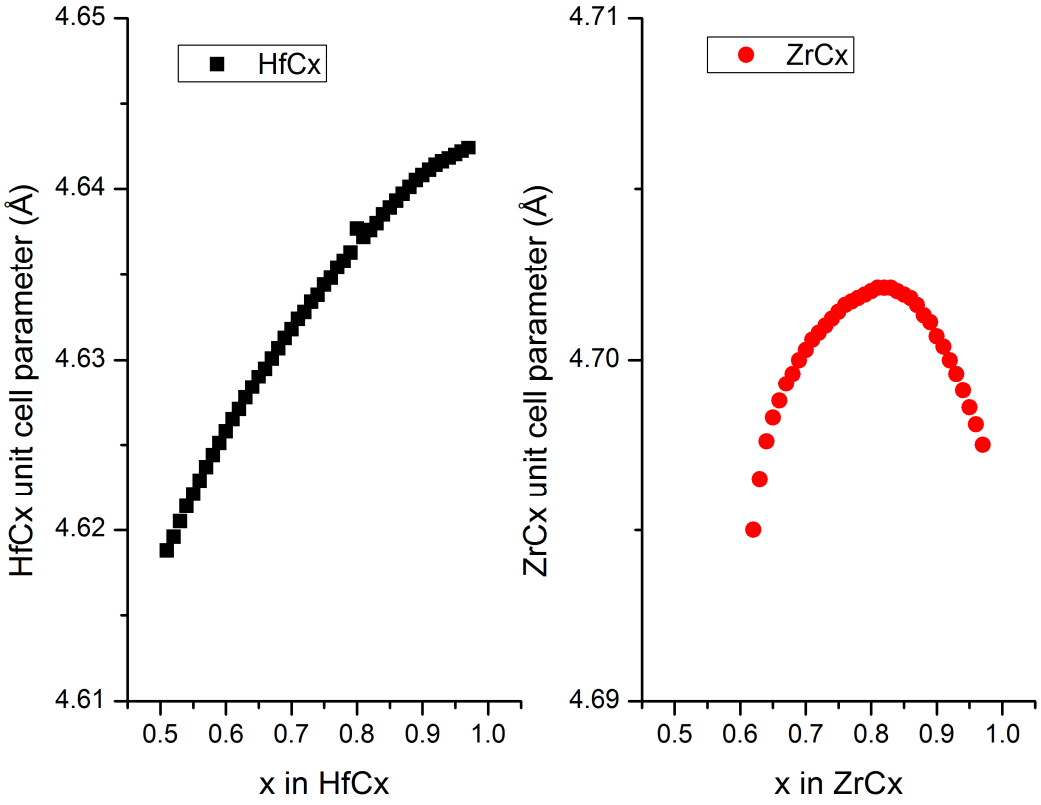

Figure S1. Dependence of unit cell parameters of substoichiometric Zr and Hf carbides from carbon content [1].

Table S3. Standard enthalpies of formation of HfC_xO_y compounds and their cell parameters measured by Kornilov *et al.* (1977)* using oxygen bomb combustion calorimetry [2].

Starting materials, synthesis conditions†	**(x) C in HfC_xO_y**	**±**	**(y) O in HfC_xO_y**	**±**	**a, Å**	**$\Delta H°f_{298.15}$ kJ/mol**	**±**
Hf, aceteylene	0.592	0.006	0.149	0.004	4.62	200	5
T max 1827-1927 °C	0.697	0.006	0.117	0.003	4.62	225	5
Pressure 10^{-3} to 10^{-4} Torr	0.727	0.006	0.103	0.007	4.622	228	5
Hf, carbon black	0.722	0.005	0.036	0.004	4.623	195	6
T max 2227-2277 °C	0.763	0.006	0.033	0.003	(4.624)‡	213	5
Pressure 10^{-4} to 10^{-5} Torr	0.787	0.006	0.055	0.003	4.633	224	6
	0.801	0.006	0.015	0.003	(4.632)‡	206	5
Hf, graphite	0.86	0.006	0.008	0.003	4.638	213	5
T max 2227-2277 °C	0.942	0.007	0.006	0.002	4.639	214	5
Pressure 10^{-4} to 10^{-5} Torr	0.982	0.006	0.017	0.002	4.641	215	3

†The dwell time was reported as several hours for all synthesis conditions.

‡These samples contained the second phase with cell parameters 4.637 and 4.640 Å respectively.

Table S4. Standard enthalpies of formation of ZrN_xO_y compounds and their cell parameters measured by Galbraikh et al. (1970) [3] using oxygen bomb combustion calorimetry.

Starting materials, synthesis conditions	(x) in ZrN_xO_y	(y) in ZrNxOy	a, Å	Hf 298.15 kJ/mol†
Zr in N_2 or NH_3	0.77	0	4.575	331
annealing	0.86	0	4.574	345
for 100 hours	0.90	0.06		398‡
at 600 °C in N_2	1		4.573	369

†uncertainties are not reported and taken as 5%.

‡365 kJ/mol after correction for oxygen assuming athermal mixture with Zr oxide.

Table S5. Heat capacities of Zr and Hf carbides reported by Turchanin (1991) [4] from high temperature drop calorimetry experiments.

T/K	Cp, J/mol/K											
	$ZrC_{0.99}$	**$ZrC_{0.76}$**	**$ZrC_{0.69}$**	**HfC**	**$HfC_{0.95}$**	**$HfC_{0.90}$**	**$HfC_{0.85}$**	**$HfC_{0.8}$**	**$HfC_{0.75}$**	**$HfC_{0.7}$**	**$HfC_{0.65}$**	**$HfC_{0.6}$**
1200	47.36	44.27	43.39	49.93	49.34	48.76	48.17	47.58	47.00	46.41	45.83	45.24
1300	48.75	45.26	44.20	50.84	50.26	49.67	49.08	48.5	47.91	47.33	46.74	46.16
1400	50.15	46.28	45.01	51.76	51.17	50.58	50.00	49.41	48.83	48.24	47.66	47.07
1500	51.54	47.31	45.82	52.67	52.08	51.5	50.91	50.33	49.74	49.16	48.57	47.98
1600	52.93	48.40	46.65	53.58	53.00	52.41	51.83	51.24	50.66	50.07	49.48	48.90
1700	54.32	49.56	47.53	54.50	53.91	53.33	52.74	52.16	51.57	50.98	50.4	49.81
1800	55.71	50.81	48.49	55.41	54.83	54.24	53.66	53.07	52.48	51.90	51.31	50.73
1900	57.10	52.19	49.63	56.33	55.74	55.16	54.57	53.98	53.4	52.81	52.23	51.64
2000	58.50	53.73	51.06	57.24	56.66	56.07	55.48	54.9	54.31	53.73	53.14	52.55
2100	59.89	55.45	52.97	58.16	57.57	56.98	56.40	55.81	55.23	54.64	54.05	53.47
2200	61.28	57.38	55.63	59.07	58.48	57.90	57.31	56.73	56.14	55.55	54.97	54.38
2300	62.67	59.54	59.37	59.98	59.4	58.81	58.23	57.64	57.05	56.47	55.88	55.30
2400	64.06	61.94	64.60	60.9	60.31	59.73	59.14	58.55	57.97	57.38	56.8	56.21
2500	65.45	64.60	71.81	61.81	61.23	60.64	60.05	59.47	58.88	58.30	57.71	57.13

Table S6. Heat capacities of Zr carbonitrides reported by Turchanin (1991) [4] from high temperature drop calorimetry experiments.

T/K	Cp, J/mol/K									
	ZrN	**$ZrN_{0.9}C_{0.1}$**	**$ZrN_{0.8}C_{0.2}$**	**$ZrN_{0.7}C_{0.3}$**	**$ZrN_{0.6}C_{0.4}$**	**$ZrN_{0.5}C_{0.5}$**	**$ZrN_{0.4}C_{0.6}$**	**$ZrN_{0.3}C_{0.7}$**	**$ZrN_{0.2}C_{0.8}$**	**$ZrN_{0.1}C_{0.9}$**
1200	53.62	53.12	52.69	52.33	52.03	51.81	51.65	51.56	51.54	51.59
1300	54.12	53.62	53.19	52.83	52.54	52.31	52.15	52.06	52.04	52.09
1400	54.61	54.11	53.68	53.31	53.02	52.79	52.64	52.55	52.53	52.57
1500	55.08	54.58	54.15	53.78	53.49	53.26	53.1	53.02	52.99	53.04
1600	55.53	55.03	54.60	54.24	53.94	53.72	53.56	53.47	53.45	53.50
1700	55.98	55.48	55.05	54.69	54.39	54.17	54.01	53.92	53.9	53.95
1800	56.42	55.92	55.49	55.13	54.83	54.61	54.45	54.36	54.34	54.39
1900	56.86	56.36	55.93	55.56	55.27	55.04	54.88	54.8	54.78	54.82
2000	57.29	56.79	56.36	55.99	55.70	55.47	55.32	55.23	55.21	55.25

Table S7. Heat capacities of Hf carbonitrides reported by Turchanin (1991) [4] from high temperature drop calorimetry experiments.

T, K	Cp, J/mol/K of $HfN_{(0.93-x)}C_xO_{0.07}$										
	x = 0	**x = 0.1**	**x = 0.2**	**x = 0.3**	**x = 0.4**	**x = 0.5**	**x = 0.6**	**x = 0.7**	**x =0.8**	**x = 0.9**	**x = 0.93**
1200	53.97	52.29	50.85	49.67	48.73	48.05	47.61	47.42	47.49	47.8	48.36
1300	54.23	52.54	51.11	49.93	48.99	48.3	47.87	47.68	47.74	48.06	48.62
1400	54.47	52.79	51.36	50.17	49.24	48.55	48.11	47.93	47.99	48.30	48.86
1500	54.71	53.03	51.59	50.41	49.47	49.79	48.35	48.16	48.23	48.54	49.10
1600	54.94	53.26	51.82	50.64	49.70	49.02	48.58	48.39	48.46	48.77	49.33
1700	55.16	53.48	52.04	50.86	49.92	49.24	48.80	48.62	48.68	48.99	49.55
1800	55.38	53.70	52.26	51.08	50.14	49.46	49.02	48.83	48.90	49.21	49.77
1900	55.6	53.91	52.48	51.29	50.36	49.67	49.24	49.05	49.11	49.42	49.99
2000	55.81	54.13	52.69	51.51	50.57	49.88	49.45	49.26	49.32	49.64	50.20

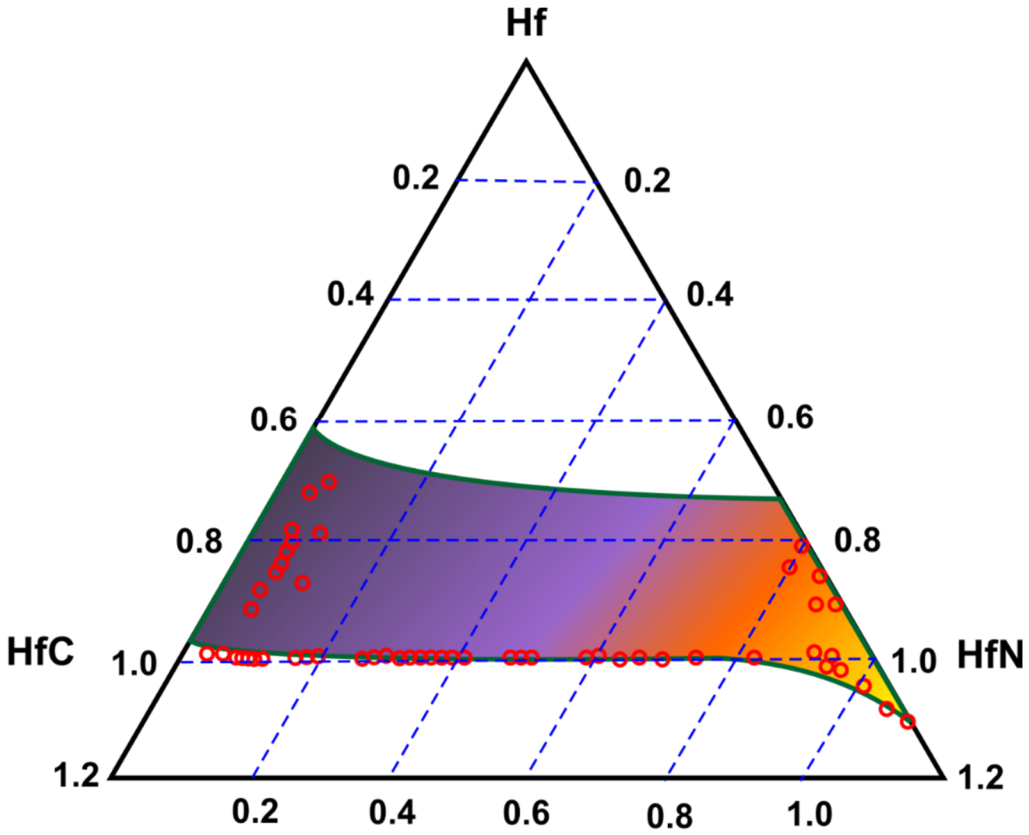

Figure S2. Compositions of NaCl-type hafnium carbonitrides in Hf-C-N system at 1500 °C and 1 atm N_2. After Brundiers (1975) [5].

Reference

1. Samsonov, G. V.; Upadhyaya, G. S.; Neshpor, V. S., *Physical Materials Science of Carbides (in Russian)*. Naukova Dumka: Kiev, 1974.
2. Kornilov, A. N.; Chelovskaya, N. V.; Zhelankin, V. I.; Shveikin, G. P., Enthalpies of formation of hafnium carbides. *J. Chem. Thermodyn.* **1977,** 9, (7), 629-42. DOI:10.1016/0021-9614(77)90088-X
3. Gal'braikh, É. I.; Kulik, O. P.; Kuznetsov, A. A.; Lyutaya, M. D.; Morozova, M. P., Enthalpy of formation of the nitrogen solid solution in α-zirconium and of zirconium nitride in their homogeneity regions. *Soviet Powder Metallurgy and Metal Ceramics* **1970,** 9, (9), 748-751. DOI: 10.1007/BF00836968
4. Turchanin, A. G.; Turchanin, M. A., *Thermodynamics of Refractory Carbides and Carbonitrides*. Metallurgiya: 1991; p 352 (in Russian)
5. Brundiers, G. D. *Herstellung, Aufbau und Eigenschaften von Hafniumverbindungen im System Hf-C-N-O*; KFK-2161; Germany, 1975; p 278. (Preparation, structure, and properties of hafnium compounds in the system hafnium-carbon-nitrogen-oxygen) http://inis.iaea.org/search/search.aspx?orig_q=RN:07230513