Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Effect of carbon vacancies on structures, mechanical properties, and chemical bonding of zirconium carbides: A first principles study

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1. Dynamical stability of the newly predicted metastable compounds

For a newly predicted structure, we need to verify its dynamical stability. Generally, a structure is dynamically stable when no imaginary phonon frequencies have been found throughout the Brillouin zone. We have computed phonon dispersion curves for the two newly predicted metastable zirconium carbides Zr_5C_4 (*P*-1) and Zr_8C_7 (*P*-1), as shown in Fig. S1 and Fig. S2. We can find that both of them are dynamically stable.

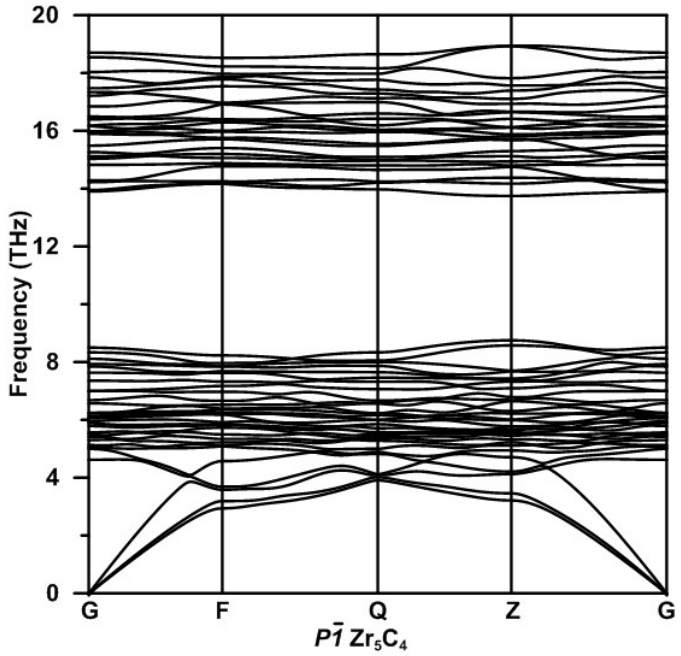

Fig. S1: Phonon dispersion curves computed for the newly predicted Zr_5C_4 (*P*-1)

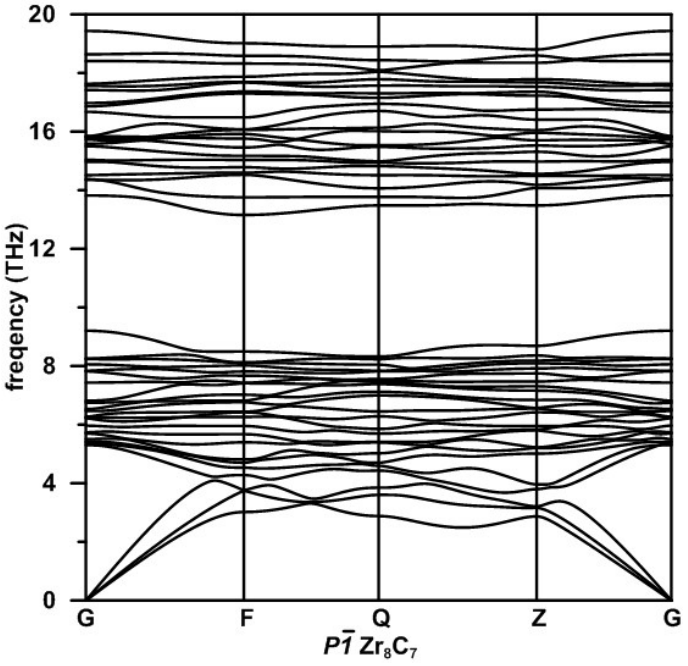

Fig. S2: Phonon dispersion curves computed for the newly predicted Zr_8C_7 (*P*-1)

2. The computed elastic constants for all the stable and metastable compounds

We have computed elastic constants for all the stable and metastable zirconium carbides (as listed in Table SI). For a structure with a given symmetry, its elastic constants matrix *C* can be used to evaluate its mechanical stability. The general stability criterion is: all eigenvalues of matrix C should be larger than zero. In the present prediction, we have discovered two new compounds Zr_5C_4 (*P*-1) and Zr_8C_7 (*P*-1). Both of them are belong to triclinic system. The eigenvalues for the two structures are listed in Table SII. We can find that both of them are mechanically stable.

Table SI The calculated independent elastic constants C_{ij} of all the predicted stable and metastable zirconium carbides.

Compounds	Zr_2C (*Fd*-3*m*)	Zr_3C_2 (*Fddd*)	Zr_4C_3 (*C*2/*c*)	Zr_5C_4 (*P*-1)	Zr_6C_5 (*C*2/*m*)	Zr_7C_6 (*R*-3)	Zr_8C_7 (*P*-1)	ZrC (*Fm*-3*m*)
C_{11}	200	301	345	369	419	385	395	496
C_{12}	105	94	104	92	83	102	110	109
C_{13}		88	89	101	87	106	104	
C_{14}				9		-5	7	
C_{15}			-10	7	3	15	4	
C_{16}				7			17	
C_{22}		299	336	375	386		397	
C_{23}		83	80	105	115		106	
C_{24}				-5			-7	
C_{25}			-1	-9	-1		5	
C_{26}				6			-6	
C_{33}		325	357	353	393	374	406	
C_{34}				1			10	
C_{35}			-8	-5	6		-14	
C_{36}				-3			-11	
C_{44}	93	110	116	142	162	155	148	151
C_{45}				-0.2			-9	
C_{46}			-7	-9	-1	-15	9	
C_{55}		100	120	142	131		146	
C_{56}				9			4	
C_{66}		110	131	135	127		156	

Table SII The eigenvalues for Zr_5C_4 (*P*-1) and Zr_8C_7 (*P*-1).

Compounds	*E*1	*E*2	*E*3	*E*4	*E*5	*E*6
Zr_5C_4 (*P*-1)	134.3682	150.8879	159.0095	288.6970	288.6970	612.7183
Zr_8C_7 (*P*-1)	125.2423	139.7452	150.8066	253.0445	281.4999	563.6535

3. Mathematical analysis about decreasing rate of bulk modulus (*dB/B*) and shear modulus (*dG/G*)

We have obtained the relationships between the concentration of carbon vacancies x and bulk modulus B and shear modulus G by fitting the computed bulk and shear moduli for all the stable and metastable zirconium carbides. We have tested different fitting models and evaluated their errors. As listed in the Table SIII, using **Linear model Poly2** is enough to get accurate fitted B and G. Thus, B decreasing rate $dB(x)/B(x)$ = (268.8 x-261.2)/(134.4x^2-261.2x+234), G decreasing rate $dG(x)/G(x)$ = (-274.2x-120.9)/(-137.1x^2-120.9x+165). Let $dB(x)/B(x)$ equals to $dG(x)/G(x)$, we get x = 0.1468. This concentration is very similar to the limits of the concentration of nonadjacent carbon vacancies 1/6, indicating nonadjacent carbon vacancies can enhance Pugh's ratio (G/B).

Table SIII The tests of fitting model for bulk modulus B and shear modulus G to carbon vacancies x.

Error	Linear model Poly1		Linear model Poly2	
	$B(x)$ = -191.7x+227.9	$G(x)$ = -191.8x+171.2	$B(x)$ = 134.4x^2-261.2x+234	$G(x)$ = -137.1x^2-120.9x+165
SSE	96.3	106.2	11.41	17.81
RMSE	4.006	4.207	1.511	1.887
Error	Linear model Poly3			
	$B(x)$ = 8.917x^3+127.9x^2-260.1x+233.9		$G(x)$ = 352.2x^3-392.9x^2-77.37x+163.9	
SSE	11.41		9.27	
RMSE	1.689		1.522	