Physical Chemistry Chemical Physics

Electronic Supplementary Information

Disorder-order and order-order phase transformations in Ta_5C_4 phases predicted by evolutionary algorithm and symmetry analysis

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Mechanical stability and elastic constants of Ta_5C_4 phases

The elastic constants c_{ij} which are directly related to the mechanical stability of Ta_5C_4 phases were calculated by VASP package [1]. The calculated elastic constants c_{ij} (Table S1) were used to estimate the mechanical stability of the ordered Ta_5C_4 phases.

Mechanical stability of the predicted vacancy-ordered Ta_5C_4 phases was determined by the Born criteria [2, 3] which are represented below as equations (S1)-(S12).

For the mechanical stability of the orthorhombic Ta_5C_4 (space group *Immm*) phase, the following equations must be satisfied:

$$c_{ii} > 0 \ (i = 1\text{-}6) \ , \tag{S1}$$
$$c_{11} + c_{22} > 2c_{12} \ , \tag{S2}$$
$$c_{22} + c_{33} > 2c_{23} \ , \tag{S3}$$
$$c_{11} + c_{33} > 2c_{13} \ , \tag{S4}$$
$$c_{11} + c_{22} + c_{33} > 2(c_{12} + c_{13} + c_{23}) \ . \tag{S5}$$

For the mechanical stability of the tetragonal Ta_5C_4 (space group *I*4/*m*) phase, the elastic constants should be satisfied to equation (S1) and also following equations:

$$c_{11} > |c_{12}| \ , \tag{S6}$$
$$c_{44} > 0 \ , \tag{S7}$$
$$(c_{11} + c_{12})c_{33} > 2c_{13}^2 \ . \tag{S8}$$

The monoclinic Ta_5C_4 (space group *C*2/*m*) phase is mechanically stable, if its elastic constants are satisfied to equations (S1), (S3), (S5) and also following equations:

$$c_{33}c_{55} > c_{35}^2 \ , \tag{S9}$$
$$c_{44}c_{66} > c_{46}^2 \ , \tag{S10}$$
$$c_{22}c_{33}c_{55} + 2c_{23}c_{25}c_{35} > c_{22}c_{35}^2 + c_{55}c_{23}^2 + c_{33}c_{25}^2 \ , \tag{S11}$$
$$2[c_{15}c_{25}(c_{33}c_{12} - c_{13}c_{23}) + c_{15}c_{35}(c_{22}c_{13} - c_{12}c_{23}) + c_{25}c_{35}(c_{11}c_{23} - c_{12}c_{13})] > $$
$$> c_{15}^2(c_{22}c_{33} - c_{23}^2) + c_{25}^2(c_{11}c_{33} - c_{13}^2) + c_{35}^2(c_{11}c_{22} - c_{12}^2) + pc_{55} \ , \tag{S12}$$

where $p = c_{11}c_{22}c_{33} - c_{11}c_{23}^2 - c_{22}c_{13}^2 - c_{33}c_{12}^2 + 2c_{12}c_{13}c_{23}$.

The relationships between the elastic constants at which the triclinic phases have mechanical stability are given in monographs [1, 2]. These relations are rather cumbersome and therefore are not presented here.

According to calculation performed, all ordered Ta_5C_4 phases are mechanically stable.

SI Table

Table S1. Calculated elastic constants c_{ij} (GPa) for predicted vacancy-ordered Ta_5C_4 phases

Elastic constants c_{ij}	Symmetry and space group			
	orthorhombic *Immm*	tetragonal *I*4/*m*	monoclinic *C*2/*m*	triclinic $P\bar{1}$
c_{11}	540.0	548.0	466.5	470.8
c_{12}	99.2	172.5	175.0	192.3
c_{13}	227.8	103.8	182.5	160.9
c_{14}	0	-34.2	0	25.9
c_{15}	0	34.2	0	-8.3
c_{16}	0	0	0.8	-17.8
c_{22}	611.4	548.0	538.5	521.4
c_{23}	133.9	0	136.9	148.9
c_{24}	0	0	0	-24.8
c_{25}	0	0	0	21.9
c_{26}	0	0	-5.45	-16.9
c_{33}	500.6	606.2	563.4	494.5
c_{34}	0	0	0	-17.0
c_{35}	0	0	0	-11.8
c_{36}	0	0	49.2	31.0
c_{44}	139.5	180.7	227.7	178.5
c_{45}	0	0	-28.6	-18.0
c_{46}	0	0	0	-19.0
c_{55}	141.8	143.4	165.7	162.6
c_{56}	0	0	0	-6.0
c_{66}	203.6	143.4	132.8	174.2

Reference

1 G. Kresse and J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169-11186.
2 *Thermodynamics of Crystals*, ed. D. C. Wallace, Wiley, New York, 1972. 484 pp.
3 M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford Univ. press, 1998. 432 pp.