The equation of state of TaC0.99 by X-ray diffraction in radial scattering geometry to 32 GPa and 1073 K

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2   GPa and 1073 K

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14   **Abstract.** We have performed in situ synchrotron X-ray diffraction experiments on

15   TaC$_{0.99}$ compressed in a diamond anvil cell along 3 isothermal paths to maximum

16   pressure (P) - temperature (T) conditions of 38.8 GPa at 1073 K. By combining

17   measurements performed in axial diffraction geometry at 296 K and in radial geometry at

18   673 K and 1073 K, we place constraints on the pressure-volume-temperature (P-V-T)

19   equation of state of TaC in a wide range of conditions. A fit of the Birch-Murnaghan

20   equation to the measurements performed in axial geometry at ambient temperature yields

21   a value of the isothermal bulk modulus at ambient conditions $K_{T0} = 305 \pm 5$ (1σ) GPa

22   and its pressure derivative $(\partial K_T / \partial P)_{T0} = 6.1 \pm 0.5$. The fit of the Birch-Murnaghan-

23   Debye model to our complete P-V-T dataset allows us to constrain the Grüneisen

24   parameter at ambient pressure $\gamma_0 = V(\partial P/\partial E)_{V0}$ to the value of 1.2 ± 0.1.

25

26   **I. INTRODUCTION**

27   Tantalum carbide TaC_x ($0.6 < x < 1$) is a B1 structured ultra-high temperature ceramic

28   (UHTC) [1]. UHTC materials have the potential to be used in different technological

29   applications because of their combined high mechanical strength, extremely good thermal

30   stability as well as its resistance to harsh chemical environments.

31   Transition metal carbides are in general among the ceramic materials with the best

32   characteristics for high temperature applications where enhanced refractory and

33   mechanical properties are required [2]. Tantalum carbide has an extremely high melting

34   temperature, low electrical conductivity and unusual mechanical behavior with respect to

35   the other B1 structured (space group $Fm\bar{3}m$) monocarbides of the group IV and V

36   transition metals (TMC) [3, 4].

37   The structural, thermodynamic and transport properties of TaC_x (in the following we will

38   use TaC except when discussing the effect of non-stoichiometry on specific physical

39   properties) have been the subject of many experimental and computational investigations

40   and part of the existing results are tabulated in several review publications together with

41   the properties of the other TMC [5-27]. In particular, the elastic properties of TaC have

42   been the subject of more than ten different experimental and computational studies [6, 15,

43   16, 28-39] exploring the effect of pressure or temperature and non-stoichiometry on the

44   tensor and the aggregate elastic moduli of single crystals or polycrystals.

45   While several computational studies provide models of the isothermal compression

46   behavior of TaC, only two experimental diamond-anvil cell studies investigate its

47   compression behavior to the multi-GPa stress range at ambient temperature [32, 37]. The

48   first study focuses on the response of micron-sized polycrystalline $TaC_{0.98}$ to compression

49   under different stress conditions, and the second explores the behavior of nanocrystalline

50   TaC under strongly nonhydrostatic stress.

51   To date there are no data on the combined effect of high-pressures, stress and -

52   temperatures on the structure and the thermoelastic properties of tantalum carbide. With

53   this study we give a first account of the compression behavior of $TaC_{0.99}$ compressed to

54   more than 40 GPa at ambient temperature and to a maximum of 38.8 GPa at 1073 K, and

55   we place quantitative constraints on the pressure-volume-temperature (PVT) equation of

56   state of this material.

57   Here we use a new approach to place quantitative constraints on the thermoelastic

58   properties of $TaC_{0.99}$. We combine the results of static compression experiments in a

59   graphite resistive heated diamond-anvil cell using in situ synchrotron X-ray diffraction in

60   radial scattering geometry (an established technique [40-46] yet never used before in

61   studies dedicated to constrain the pressure-volume-temperature equation of state) with

62   those from axial geometry at room temperatures. The use of high-temperature high-

63   pressure radial diffraction geometry in combination with a theory of non-hydrostatic

64   lattice strains allows us to quantitatively constrain the departure from hydrostatic stress

65   conditions, which is not straightforward in experiments performed in axial geometry.

66   This is particularly relevant for stiff samples such as TaC when they bridge between the

67   culets of the two diamond anvils under combined high pressure and high temperature. In

68   addition the experimental approach used here allows us to measure high temperature

69   volume compression along strictly isothermal compression paths at moderately high

70   temperatures, which is difficult with laser-heated diamond anvil-cell experiments, thus

71   producing the best suited dataset for P-V-T equation of state fitting.

72

73   **II. MATERIALS AND METHODS**

74   A. Sample material

75   The starting material for all experiments presented here is a powder of TaC$_{0.99}$ (with

76   nominal stoichiometric TaC composition) produced by American Elements©. We have

77   determined the chemical composition of our starting material by measuring its unit-cell

78   volume by X-ray diffraction at the German Research Centre for Geosciences (GFZ) using

79   a STOE Stadi P diffractometer with Cu Kα radiation monochromatized by a Ge(111)

80   crystal. Two separate amounts of sample were mixed with ~10 wt% Si standard (NIST

81   640d) as an internal calibrant. The average of the two measurements yields a unit-cell

82   parameter $a_0 = 4.4555 \pm 0.0007$ Å. This value corresponds to a composition of TaC$_{0.99}$

83   based on the calibration by Bowman [8]. The unit cell parameter of our sample is

84   equivalent within uncertainty to the results of neutron diffraction measurements of a

85   disordered stoichiometric TaC [9] and 3σ larger (rather than smaller, as expected) than a

86   more recent neutron diffraction study of nominally stoichiometric TaC [10].

87

88   B. High-pressure synchrotron X-ray diffraction in axial geometry

89   In these experiments the axis of the diamond anvils is parallel to the incident X-ray beam.

90   TaC$_{0.99}$ was compressed quasi-hydrostatically in a symmetric piston-cylinder type

91   diamond anvil cell [47] with 300 μm culet diamonds. Fine sample powder (with less than

92   1μm average grain-size) was loaded in a 150 μm wide cylindrical chamber drilled in a

93   250 μm thick rhenium disk pre-indented to a thickness of 30 μm. Neon gas was loaded as

94   a pressure transmitting medium using the gas-loading facility from Core Labs located at

95   PETRA III and operated by the Extreme Condition Science Infrastructure. A ruby sphere

96   and a ∼ 5 μm speckle of gently packed gold powder were used as internal pressure

97   standards [48, 49]. The diamond anvil cell was compressed remotely with a gas-

98   membrane system. X-ray diffraction images were collected at the general purpose

99   experiment table of Extreme Conditions Beamline (ECB, P02.2) of the 3rd generation

100   light source PETRA III at DESY, Hamburg, Germany. The monochromatic incident X-

101   ray radiation had a wavelength of 0.2966 Å. The beam was focused to a spot size of 3μm

102   (vertical) by 8 μm (horizontal) full width at half maximum by means of Compound

103   Refractive Lenses (CRL). X-ray diffraction images were collected with a Perkin Elmer

104   XRD1621 flat panel detector at 420 mm distance from the sample. The sample to

105   detector distance and tilting angles of the detector were calibrated using a CeO$_2$ standard

106   from the National Institute of Standards and Technology (NIST, 674b). Twenty X-ray

107   diffraction images were collected at pressures between 5.1 GPa and 43.6 GPa, including

108   3 images collected during decompression. The exposure time for each image was 20 s.

109   The images were analyzed with the Fit2d software package [50]. Le Bail fit [51] of the

110   integrated spectra were performed with the software MAUD [52] to determine the unit

111   cell parameter a (TaC crystallizes in the cubic system in the space group $Fm\bar{3}m$). A

112   typical X-ray diffraction image and the result of the Le Bail fit are shown in Figure 1.

113   The conditions and the results of the room temperature compression experiments are

114   reported in Tables I and II.

115

116   C. Simultaneous high-pressure high-temperature synchrotron X-ray diffraction in radial

117   scattering geometry

118   Two series of measurements were performed in radial scattering geometry at the general

119   purpose experiment table of the ECB. In these experiments the axis of the diamond anvils

120   is perpendicular to the incident X-ray beam, passing through an X-ray transparent sample

121   chamber, made of a mixture of amorphous boron and epoxy.

122   The setup for these experiments is based on a modified Mao-Bell piston-cylinder type

123   diamond anvil cell equipped with a graphite resistive sandwich heater for high-

124   temperature experiments [53]. Pressure in the diamond anvil cell is controlled remotely

125   by a gas membrane system. For temperature measurements two type-R thermocouples are

126   placed in contact with the diamond at short distance from the culets. The diamond anvil

127   cell is placed in a vacuum vessel (capable of maintaining 10^{-4} mbar pressure during the

128   experiments) to protect diamonds, the metallic parts of the diamond anvil cell and heater

129   setup from oxidation [54].

130   $TaC_{0.99}$ powder with a grain size < 1 μm was loaded in 50 μm diameter cylindrical

131   chambers laser-drilled in amorphous boron – epoxy gaskets of 380 μm diameter and 50

132   μm thickness. With such a narrow sample-chamber the entire sample remains as close as

133   possible to the center of the diamond culets, where stress gradients are low and where

134   stress and strain fields are close to ideal axial symmetry that is required in the

135   interpretation of X-ray diffraction experiments in radial scattering geometry (see section

136   II.D). The ceramic gaskets are supported by a kapton ring. In all the experiments the

137   diameter of the diamond culets was 300 µm and no pressure transmitting medium was

138   employed.

139   In the two high-temperature experimental runs a 5-10 µm wide fragment of less than 5

140   µm thick Au foil was placed above the sample as a pressure calibrant. The two high-

141   temperature experimental runs were performed using a monochromatic X-ray beam of

142   0.4847 Å wavelength with an identical focus spot-size as for the axial diffraction

143   experiment but slightly different sample to detector distance of 405 mm based on the

144   same calibration approach as for the axial diffraction experiment.

145   The exposure time for all images in the radial X-ray diffraction experiments was 4s. The

146   images were processed using Fit2d [50]. Each image was integrated in 5° azimuthal (ψ)

147   sectors, for a total of 72 patterns per image. The sets of patterns were further analyzed

148   with MAUD software package [55] to determine structural parameters.

149   In ideal conditions, the geometry of the diamond anvil cell imposes a cylindrical

150   symmetry of stress and strain at the center of the sample chamber (i.e. along the culets'

151   axial direction). The stress state far from the center of the culets is more complex [56].

152   For this reason at each pressure step the optimized position was determined by X-ray

153   absorption scans along the vertical and horizontal direction. An additional diffraction

154   image of gold was collected at each compression step for pressure calibration at high

155   temperatures [49].

156   In both the 673 K and 1073 K runs the sample was compressed at ambient temperature to

157   2.5 ± 1 GPa and then progressively heated to the target temperature at an average rate of

158   3.2 °C/min and 4.6 °C/min, respectively. A total of 47 X-ray diffraction images were

159 collected along two isotherms at 673 K and 1073 K. The parameters of all the

160 experimental runs are reported in Table I.

161

162 D. Data analysis of radial diffraction data with MAUD

163 All radial X-ray diffraction images were analyzed using MAUD software package.

164 MAUD determines both crystal structure parameters, and texture by combining Rietveld

165 full-spectrum fitting and a selection of models to describe crystallite sizes, microstrains,

166 macroscopic stress and the crystals' preferred orientation [53, 57].

167 In radial X-ray diffraction experiments the sample is subject to strongly non-hydrostatic

168 macroscopic stress because it is loaded without any soft pressure transmitting medium.

169 The X-ray diffraction images display anisotropic strains caused by the uniaxial stress

170 applied to the sample. This results in non-circular Debye diffraction rings, with their

171 ellipticity being related to the amount of deviatoric stress and the elastic moduli of the

172 sample material. Specialized theories to describe non-hydrostatic crystal strains have

173 been developed to analyze the X-ray diffraction images collected from samples

174 compressed in the diamond anvil cell and other high-pressure devices [57-59]. In our

175 analysis here we are interested in the study of the (volume) compression of TaC, and we

176 correct for the effect of nonhydrostaticity by using the theory developed by Singh [58].

177 Here we assume that the $TaC_{0.99}$ polycrystalline aggregate sample behaves as an

178 elastically isotropic material. Following the formulation presented by Singh [58] for the

179 isotropic aggregate case:

$$d_d(hkl) = d_p(hkl)[1 + (1 - 3cos^2\psi)Q], \qquad (1)$$

181   where $d_d(hkl)$ is the d-spacing of the (hkl) lattice planes family as determined in the

182   spectrum integrated at an angle ψ measured anticlockwise from the compression

183   direction. $d_p(hkl)$ is the d-spacing under hydrostatic stress (corresponding to pressure p),

184   and Q is a measure of the strain due to the deviatoric component of the stress. For

185   isotropic aggregates of elastically anisotropic materials, and assuming that stress is

186   homogeneous in the aggregate Singh [58] derives:

187
$$\langle Q \rangle = t\,(1 + v)/3E = t/6G, \qquad (2)$$

188   Where $\langle Q \rangle$ is the isotropic aggregate Q, averaged on all the diffracting lattice families

189   (see equation (1)), $t = \sigma_3 - \sigma_1$ is the difference between the normal stress along the

190   compression axis and perpendicular to it, v is the average Poisson's ratio, E is the

191   Young's modulus of the isotropic aggregate sample, and G is the isotropic aggregate shear

192   modulus. The model of Singh [58] is incomplete for aggregates subject to plastic

193   deformation and with large density of defects [60]. However, equation (1) has been

194   shown to be useful to describe such experimental data, extract average stress levels [61],

195   and model plastic behavior of materials using more advanced methods [62].

196   The unit cell parameter a corresponding to the hydrostatic stress component is

197   determined from the spectrum at $\psi = 54.7$ degrees. The implementation of the model

198   available in MAUD allowed us to fix the values of v and E and refine the values of σ_3

199   and σ_1 to fit the observed d-spacings. We calculated the value of $\langle Q \rangle$ by using equation

200   (2). This can finally be easily converted (see equation (1)) into the non-hydrostatic stress

201   contribution to the uncertainty on the unit cell parameter. The uncertainties due non-

202   hydrostatic conditions are in average of the order of 10^{-2} Å, substantially larger than the

203   estimated uncertainties on the values of the unit cell parameter refined with the full

204   spectrum fit which are of the order of 10^{-4} Å.

205   A typical X-ray diffraction image collected in radial scattering geometry is shown in

206   Figure 2(a). The unrolled sequence of spectra integrated at 5 degree azimuthal-angle

207   steps (see methods) is presented in Figure 2(b) together with the fit result.

208   In both the experiments performed at 673 K and 1073 K pressure was determined by

209   fitting the unit cell parameter of gold, loaded together with the sample in the sample

210   chamber. The analysis of X-ray diffraction of gold was performed similarly to that of the

211   sample material itself. The stress/lattice strain analysis generally gave results of

212   deviatoric stress comparable with those of the $TaC_{0.99}$ sample. In some few cases the fit

213   of stress and lattice strain of gold did not converge to consistent results due to lower than

214   average gold diffraction signal.

215   The 3 X-ray diffraction images collected at 6.0, 6.8 and 8.2 GPa at 673 K and the 5 ones

216   collected at 1073 K from 32.9 to 38.8 GPa show a deviation from the ideal geometry,

217   with a maximum of lattice strains in a direction tilted with respect to the diamond anvil

218   axis (Figure 3). Non-ideal stress conditions are typically due to gasket partial failure at

219   the highest pressures (as in the case of the 1073 K isotherm) or, less frequently, at the

220   lowest pressures, at the first contact between the diamond culets and the ceramic gasket

221   (as in the case of the 673 K isotherm). Nevertheless, we performed a full analysis also of

222   these images and we will discuss the results below.

223   All parameters determined by Rietveld analysis of the diffraction images of $TaC_{0.99}$ in the

224   two radial X-ray diffraction experimental runs are reported in Table II.

225

226 E. P-V-T equation of state analysis

227 A third order Birch-Murnaghan P-V equation of state [63] was fitted to the unit cell

228 volumes of $TaC_{0.99}$ measured in the experiments performed in axial geometry and quasi-

229 hydrostatic stress. Pressures were determined from the unit cell volume of gold loaded in

230 the diamond anvil cell together with the sample [49]. The pressure - volume data were

231 weighted by the pressure uncertainties on the measurements of both gold and $TaC_{0.99}$

232 propagated from the uncertainties of their respective experimentally determined unit cell

233 volumes.

234 The three coefficients of the third order Birch-Murnaghan equation are the unit cell

235 volume at ambient conditions V_0, the isothermal bulk modulus at ambient conditions K_{T0}

236 and its isothermal pressure derivative at ambient conditions $(\partial K_T / \partial P)_{T0}$. We fixed the

237 value of V_0 to the one we measured at the GFZ (see above) and we refined the values of

238 K_{T0} and $(\partial K_T / \partial P)_{T0}$. The individual data points used in the fit are reported in Table III

239 ("TaC-Ne"). In the fit we did not consider all the data points collected in decompression,

240 however we will mention, in the discussion, their effect on the fit results. After the first

241 decompression step the piston and cylinder of the diamond anvil cell were jammed. We

242 observed a sudden decrease of sample (and Au standard) unit cell volume between each

243 of the decompression points. The decompression volume – pressure data do not plot on

244 the compression dataset, even though they overlap within reciprocal pressure

245 uncertainties. Our interpretation is that, due to the sudden stress release, the stress field

246 applied to the sample was different with respect to that generated by the smooth stress

247 increase in compression, and the anomalous stress condition affected the pressure

248 determination. The last data point, collected at 1 bar after complete pressure release,

11

249   overlaps with the ambient conditions X-ray diffraction measurement and refinements

250   performed at the GFZ (see Figure 4).

251   The pressure volume data of $TaC_{0.99}$ collected in radial diffraction geometry along the

252   two high temperature isotherms at 673 K and 1073 K were used to fit the parameters of

253   the Birch-Murnaghan-Debye P-V-T equation of state (e.g. [64]). Pressures were

254   determined from the measured unit cell volume of gold loaded in the diamond anvil cell

255   together with the sample. Error propagation of the uncertainties on sample and gold

256   experimental unit cell volumes was performed using the same strategy as for the room

257   temperature quasi-hydrostatic experimental dataset. We additionally weighted the data of

258   the high temperature runs (performed without soft pressure transmitting medium) by

259   propagating the additional volume strain caused to the uniaxial stress present in the

260   sample chamber (see section about Q – lattice strains analysis). The uncertainty on

261   temperature in the experimental setup used in this study is estimated to be $\pm$ 20 K at 673

262   K and $\pm$ 60 K at 1073 K [53].

263   The coefficients of the Birch-Murnaghan-Debye equation are V_0, K_{T0} and $(\partial K_T/\partial P)_{T0}$

264   for the reference isotherm, which we fixed to be the ambient temperature isotherm. Three

265   thermal parameters were refined: the Grüneisen parameter at ambient conditions γ_0, its

266   logarithmic volume derivative $q = (\partial \ln \gamma/\partial \ln V)_T$, and the Debye temperature at

267   ambient conditions θ_0. Due to our limited dataset we fixed the initial unit cell volume of

268   the reference isotherm (V_0) to our own measurement result and the value of θ_0 to 567 $\pm$

269   10 K which is the average of the available literature data [19, 24, 30, 31, 36, 39]

270   excluding the two extreme values [34, 37]. We thus refined the value of q and γ_0, for

271   which the extant published results are in strong disagreement [17, 31, 36].

12

272   The whole dataset used to fit the parameters of the equation of state of TaC$_{0.99}$ are

273   reported in Table II.

274

III. RESULTS

276   A. Isothermal equation of state of TaC$_{0.99}$ at 296 K

277   The unit-cell volumes determined in the quasi-hydrostatic experiment are reported in

278   Table II. The compression curve is plotted in Figure 4. The third order Birch-Murnaghan

279   fit of our data yields $K_{0T} = 305 \pm 5$ GPa and $(\partial K_T/\partial P)_{T0} = 6.1 \pm 0.5$, where K_{0T} is the

280   initial bulk modulus and $(\partial K_T/\partial P)_{T0}$ is its initial pressure derivative. We performed our

281   fit by fixing V_0 (the initial unit-cell volume) to the value of 88.478 Å^3 based on our

282   measurement at ambient pressure. The root mean square (RMS) misfit of the pressure

283   dataset is 0.29 GPa. We tested the effect of including the three decompression data (these

284   collected at 38.9, 32.0 and 18.8 GPa) in the fitted dataset. The fitted coefficients are

285   insensitive, within estimated uncertainties, to the inclusion of the decompression data.

286   However, the RMS misfit increases by more than 20% by adding these three data points,

287   and we decided to exclude them in our final fit (see Table II). The model isothermal

288   compression curve is plotted as a solid line in Figure 4.

289

290   B. P-V-T equation of state of TaC$_{0.99}$

291   The high-temperature unit-cell volumes dataset (Table II) combined with the parameters

292   of the ambient temperature isotherm were used to fit the thermal coefficients of a Birch-

293   Murnaghan-Debye equation of state. We did not include in the dataset the data collected

294   at 6.0, 6.8 and 8.2 GPa and 673 K and the 5 ones collected at 1073 K from 32.9 to 38.8

295   GPa (see also discussion). In the fit we fixed the value of θ_0 to the value of 570 ± 10 K

296   averaged between the available literature data (see methods above). The fit yields an

297   initial value of the Grüneisen parameter $\gamma_0 = 1.2 \pm 0.1$. The value of the logarithmic

298   pressure derivative of the Grüneisen parameter (q) is poorly constrained by the current

299   dataset and the best fit value is $q = 1 \pm 2$. The RMS pressure misfit of the full high

300   temperature dataset is equal to 0.46 GPa. The complete set of coefficient of the pressure-

301   volume-temperature equation of state of $TaC_{0.99}$ based on our experimental results is

302   reported in Table III. The experimental unit-cell volumes and the model isotherms at 296

303   K, 673 K and 1073 K are plotted in Figure 5.

304

305   **IV. DISCUSSION**

306   A. Isothermal equation of state of $TaC_{0.99}$ at 296 K

307   The values of $K_{0T} = 305 \pm 5$ and $(\partial K_T/\partial P)_{T0} = 6.1 \pm 0.5$ constrained by our new quasi-

308   hydrostatic dataset compare well with the available computational and experimental

309   results for TaC_x (Table IV).

310   Several ab initio DFT computational studies have investigated the elastic properties of

311   TaC [6, 13, 15, 18, 33-39]. The values of the ambient pressure bulk modulus are

312   generally similar in all the studies when the same approximation is used for the

313   exchange-correlation electronic interaction. The average for the studies using the

314   generalized gradient approximation (GGA) is 315 ± 16 GPa and overlaps with our result

315   within reciprocal 1σ uncertainties. One of the computational studies [33] combines DFT

316   calculations and experimental ultrasonic interferometry data, for only two of the three

317   elastic stiffness coefficients of TaC. Using the elastic anisotropy expressed as the Zener

14

318   anisotropy ratio $A = 2C_{44}/(C_{11} - C_{12})$ [65], from their calculations we can estimate the

319   value of the experimental bulk modulus $K_{0S} = 310$ GPa, which agrees with our result

320   within 1σ. Here we point out that the difference between the isothermal bulk modulus

321   K_{0T} and the isentropic bulk modulus K_{0S} expressed by the thermodynamic relationship

322     $K_{0S} = K_{0T}(1 + \alpha\gamma T)$(where α is the thermal expansion coefficient, and γ is the

323   Grüneisen parameter) in the case of TaC is of the order of 3 ± 1 GPa, which is

324   comparable with the uncertainties of all the existing experimental studies (Table IV).

325   Our best fit K_{0T} is at the lower end of the values of isothermal and isentropic bulk

326   modulus reported in the literature except for a single-crystal ultrasonics study of TaC$_{0.90}$

327   [29] and a neutron inelastic scattering study of single-crystal TaC [17] which yield $K_{0S} =$

328   217 ± 12 GPa and $K_{0S} = 283$ GPa, respectively. The three studies performed on TaC$_{0.99}$,

329   present values of the isentropic bulk modulus K_{0S} between 345 GPa, and 317 GPa [28,

330   30, 66] all calculated by extrapolation to full density of ultrasonic experimental studies of

331   porous ceramic materials. If we consider all the available data from elasticity studies

332   including a study of TaC$_{0.98}$ [31] the average value of 335 ± 13 GPa is compatible with

333   our fitted value only at 3σ uncertainty level.

334   Only three experimental and three computational studies investigated the pressure

335   dependence of the elastic moduli of TaC$_x$ [16, 31-33, 36, 37]. The pressure derivatives

336     $(\partial K_T/\partial P)_{T0}$ based on experimental studies [31, 32, 37] are equal to 4.97 ± 0.27, $4.0 \pm$

337   0.4 and 4 respectively, and are substantially different from our result. However, the

338   pressure derivative presented in [31] is calculated from ultrasonics pulse-echo

339   measurements of a compressed porous sample without direct measurements of the sample

340   volume. The value reported by [37] is based on a high-pressure X-ray diffraction study of

341   nano-particle TaC, which could have a different elastic behavior with respect to the bulk

342   material (see for instance the case of MgO [67]), and it has been fixed in the data

343   analysis. The results of [32] are based on a similar approach as the one used in the present

344   study and the large disagreement deserves a more detailed explanation. Liermann and

345   coauthors [32] performed high-pressure X-ray powder diffraction of $TaC_{0.98}$ compressed

346   in the diamond anvil cell using Al as a pressure transmitting medium. Even though Al is

347   a metal with low shear modulus at ambient conditions, it represents a strong pressure

348   medium if compared to Ne at pressures of tens of GPa. The use of strong pressure media

349   unavoidably produces deviatoric stress in the sample chamber. In axial X-ray diffraction

350   geometry the crystallites which contribute to the measured signal are those with

351   diffracting vectors (the directions normal to the diffracting lattice planes) close to

352   perpendicular to the diamond axes, and thus subject to deviatoric extension (relative to

353   the ideal hydrostatic strain) [58]. This causes underestimation of volume compression and

354   overestimation of the material bulk modulus [67, 68]. In addition to this, the value of bulk

355   modulus and pressure derivative at ambient conditions obtained by fitting high-pressure

356   X-ray diffraction results suffer from trade-offs between the two coefficients of the fitted

357   equation of state [69]. In order to better compare the results of the two studies we have

358   plotted the difference between the P-V isotherms calculated using the two sets of

359   parameters and a common starting volume (Figure 6). This procedure corresponds to

360   comparing pressures along the two isotherms at the same values of compression. The

361   difference between the two compression curves is within three times the average

362   uncertainty of our data if we include the error propagated from the unit-cell volume

363   uncertainty. If we consider that the experimental uncertainties on pressure and unit-cell

16

364   volume in [32] are of the same order of magnitude as the one in our dataset, the

365   disagreement between the two isothermal equations of state is within 2σ reciprocal

366   uncertainties. The similarity between the compression curves of $TaC_{0.99}$ and $TaC_{0.98}$

367   suggests that, within experimental uncertainties, the isothermal compressibility of TaC_x at

368   300 K is only marginally sensitive to low levels of nonstoichiometry ($0.98 \le x < 1$).

369   The pressure derivative of the bulk modulus from the four ab initio computational studies

370   with local density approximation (LDA) [33], generalized gradient approximation (GGA)

371   [36] and with both approximations [16, 37] is in all cases substantially smaller (between

372   29% and 42%) than our result. However, this is partially compensated by their larger bulk

373   modulus at room pressure. The discrepancy between our experimental results and ab

374   initio computations could be due to the presence, in our sample material, of a complex

375   defect structure in addition to slight non-stoichiometry, which includes dislocations, grain

376   boundaries and microstrains associated to them. Indeed it has been observed that carbon-

377   defective TaC_x ceramics show higher mechanical strength than stoichiometric TaC [3].

378   The characterization of defects states and their energetics in TaC has been subject of

379   several computational and theoretical studies [70, 71]. A recent study has shown that

380   increasing C vacancies concentration reduces the elastic moduli of TaC_x [72]. However,

381   it is not yet clear what effect this deficiency has on the pressure dependence of bulk

382   modulus. The isothermal compression curves of all the existing high-pressure studies of

383   TaC_x [16, 31-33, 36, 37] are calculated with the same procedure as for [32] (see above)

384   and compared with ours in Figure 6.

385

386   B. P-V-T equation of state of $TaC_{0.99}$

387   Our full high-pressure / high-temperature dataset places a strong constrain on the value of

388    $\gamma_0 = 1.2 \pm 0.1$. In the framework of the Birch-Murnaghan-Debye model this coefficient is

389   the thermodynamic Grüneisen parameter at ambient conditions. This value is obtained by

390   fitting both our full dataset, or after removing the 3 data points at 6.0, 6.8 and 8.2 GPa

391   and 673 K and the 5 data for 32.9, 34.9 36.1, 37.9 and 38.8 GPa and 1073 K due to their

392   non-ideal geometry (see section 2. Materials and Methods). Our best-fit value of

393   γ_0 compares very well with the value of the elastic Grüneisen parameter $\gamma_{el} = 1.22$

394   determined for polycrystalline $TaC_{0.98}$ by ultrasonic techniques [31]. However, the elastic

395   Grüneisen parameter is the average value of the volume dependence of the acoustic

396   phonon frequencies at the Brillouin zone center, a parameter which is different from the

397   thermodynamic Grüneisen parameter $\gamma_{th} = \alpha K_S / (\rho C_p)$ (where α is the volume thermal

398   expansion coefficient, K_S is the isentropic bulk modulus, ρ is density and C_p is the

399   specific heat at constant pressure) which controls the thermal pressure contribution in the

400   P-V-T equation of state. The value of the thermodynamic Grüneisen parameter at

401   ambient conditions calculated from the published thermoelastic properties of TaC_x (Table

402   V) ranges between 1.47 and 2.34, that is 30% to 90% larger than the best-fit value to our

403   experimental dataset. The reason of this difference is clearly due to the limitations of the

404   Birch-Murnaghan-Debye model to describe the thermal energy contribution in $TaC_{0.99}$.

405   The high temperature study of the elastic properties of $TaC_{0.99}$ by Jun and Shaffer [30]

406   shows that the thermodynamic Grüneisen parameter has very strong temperature

407   dependence below 600 K at ambient pressure with a decrease from 1.48 at 300 K to 1.2 at

408   600 K, and then it remains almost constant at the value of 1.2 at temperatures as high as

409   1500 K. On the opposite, Peng et al. [36] who use the Debye model and a quasi-harmonic

410 approximation obtain γ slowly increasing with temperature at ambient pressure (Figure

411 7).

412 The quasi-harmonic approximation underlying our equation of state assumes that γ is not

413 explicitly temperature dependent (it is indeed temperature dependent through its volume

414 dependence). This approximation seems to hold for $TaC_{0.99}$ at temperatures above 600 K.

415 The result of the fit to our 673 K and 1073 K isotherms constrains an effective high-

416 temperature value of the ambient pressure thermal Grüneisen parameter, which is more

417 consistent with the results of high temperature ultrasonics measurements [30] rather than

418 room temperature ultrasonics [30, 31] or computations [36].

419 The value of q, the logarithmic volume derivative of the Grüneisen parameter, is poorly

420 constrained by our high-temperature dataset. The best-fit value of q is strongly affected

421 by the highest pressures data along the 1073 K isotherm. The fit to our full dataset yields

422 $q = -0.3 \pm 1.4$, while excluding the non-ideal data points at 32.9, 34.9 36.1, 37.9 and 38.8

423 GPa at 1073 K from the fit yields $q = 1 \pm 2$ (see also results). The average RMS misfit of

424 the full dataset (50 data points) is 0.46 GPa, that of the non-ideal 5 data points is 0.59

425 GPa while that of all the others is 0.44 GPa. The non-ideal data points have a 34% higher

426 disagreement with the fit than all the rest of the dataset. We interpret this as a systematic

427 bias probably connected to the non-ideal geometry in these measurements, and we

428 consider the result of the analysis of the reduced dataset as our best fit result. The fit

429 results are instead unaffected by including or excluding the 3 non-ideal data points at 6.0,

430 6.8 and 8.2 GPa along the 673 K isotherm. Based on the overall fit of the model

431 isotherms at 673 K and 1073 K, a value of q close to unity is a good approximation of the

432   logarithmic volume sensitivity of γ in the high temperature regime (T > 600 K). This

433   corresponds to:

434                              $$\gamma(V) \cong \gamma_0^{HT}(V/V_0), \qquad\qquad\qquad (4)$$

435   where γ_0^{HT} is the high-temperature, ambient pressure value of $\gamma = 1.2 \pm 0.1$ based on our

436   fit (see discussion above), V represents volume and V_0 the volume at ambient conditions.

437   In conclusion, our P-V-T model is able to successfully describe the pressure – volume –

438   temperature relationship for $TaC_{0.99}$ at 296 K and in the high-temperature range between

439   673 and 1073 K at pressures as high as 35 GPa, while we expect that it fails to describe

440   the high-pressure behavior of $TaC_{0.99}$ in the ~300-600 K temperature regime, especially

441   at low pressures. The parameters for the high-temperature equation of state of $TaC_{0.99}$ are

442   reported in Table III. The extant published results for TaC_x are reported for comparison

443   in Tables IV and V.

444

445   **V. CONCLUSIONS**

446   Our extensive experimental investigation gives new information about the compression

447   behavior of $TaC_{0.99}$ under very high pressures and temperatures in the diamond anvil cell.

448   a) We have constrained the parameters of the P-V-T equation of state of $TaC_{0.99}$ to 1073

449   K and 32 GPa. The ambient pressure derivative of the bulk modulus is substantially

450   higher (50%) with respect to previous studies at the same composition. The

451   thermodynamic Grüneisen parameter refined from our results is lower than the available

452   data at ambient conditions, and it seems to be consistent with the experimental high

453   temperature limit. The approach used here of determining isothermal EOS data from x-

454   ray diffraction data collected in the radial diffraction geometry under nonhydrostatic

455 conditions is novel and shows the potential of this technique, in particular the use of

456 ceramic gaskets that are more stable at higher temperatures and the lack of a hydrostatic

457 compression medium. Thus, the technique is ideally suited to characterize the thermal-

458 elastic properties of hard materials such as transition metal carbides.

459

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469

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584

585

586   Figure captions

587   Figure 1. X-ray diffraction of $TaC_{0.99}$ compressed in Ne pressure transmitting medium to

588   19.7 GPa at ambient temperature. (a) X-ray diffraction image; (b) Integrated pattern

589   and LeBail calculated best fit spectrum. The bars underneath the pattern are the

590   calculated positions of the diffraction peaks of TaC and of gold (used as an internal

591   pressure standard). The misfit is also plotted as the difference between calculated and

592   observed amplitudes.

593   Figure 2. Radial X-ray diffraction of $TaC_{0.99}$ compressed without pressure transmitting

594   medium to 29.4 GPa at 1073 K. (a) X-ray diffraction image; (b) Sequence of patterns

595   integrated from 5° azimuthal sectors and the fit model calculated by MAUD software

596   (the arrows indicate the compression direction parallel to the diamond anvils axes).

597   Figure 3. Example of radial X-ray diffraction measurement in non-ideal sample

598   geometry. (a) Sequence of azimuthally integrated patterns from the radial X-ray

599   diffraction image collected at 38.8 GPa and 1073 K. The direction of the diamond

600   axes (red arrow) does not correspond to that of maximum strain of the sample (white

601   arrow); (b) Ideal case (29.4 GPa and 1073 K) the direction of maximum strain

602   corresponds to the diamond axis direction.

603   Figure 4. Isothermal compression of $TaC_{0.99}$ at ambient temperature (296 K). The dataset

604   used for the analysis is that of experiment "TaC-Ne" (see text). The data collected in

605   decompression were not used for the fit of the P-V equation of state.

606   Figure 5. P-V-T compression behavior of $TaC_{0.99}$. The data used for fitting are colored as

607   a function of the experimental temperature following the color scale displayed in the

608   legend. The curves are the best-fit model P-V isotherms at the temperatures of the 3

27

609   datasets (296 K, 673 K, 1073 K). The white-filled symbols correspond to data points

610   in non-ideal geometry (see text), which were not used for the fit.

611   Figure 6. Comparison of the 296 K P-V equation of state of $TaC_{0.99}$ with the other

612   available models for TaC_x compositions. The disagreement is expressed as the

613   difference between the pressures calculated for the different models and our equation

614   of state at the same values of Eulerian strain. The differences are plotted versus the

615   pressure calculated with our equation of state (in abscissa). In the legend "exp"

616   indicates experimental studies, "DFT" indicates computational studies using density

617   functional theory.

618   Figure 7. Temperature dependence $TaC_{0.99}$ thermodynamic Grüneisen parameter at

619   ambient temperature. The results from our P-V-T are compared with the other

620   available results from experimental and computational studies.

621

622   Tables titles

623   Table I. Experimental condition of the four X-ray diffraction datasets. "Cold compr." is

624   the maximum sample pressure before starting heating.

625   Table II. Summary of the all the experimental results from all the three runs. "stdev P +

626   V-TaC" is the complete uncertainty on pressure including the propagation of the

627   uncertainty on the unit-cell volume of $TaC_{0.99}$. "<Q>" is the isotropic aggregate value

628   of Q, a measure of the strain due to the deviatoric component of the stress applied to

629   the sample (see main text). "PV fit" indicates whether the data points were used or

630   not in the isothermal (296 K) P-V equation of state fit. "PVT fit" indicates whether

631   the data points were used or not in the P-V-T equation of state fit.

632   Table III. Best fit parameters of the P-V-T equation of state of $TaC_{0.99}$ based on our

633   experimental data.

634   Table IV. Comparison of our best-fit thermoelastic parameters for $TaC_{0.99}$ and all the

635   available literature data. "E" is the isotropic aggregate Young's modulus. "Poisson's"

636   is the isotropic aggregate Poisson's ratio. All the parameters refer to ambient

637   conditions. ^{Y}The elastic coefficients are not presented in the original paper.

638   *Parameter fixed in the analysis of the data.

639   Table V. Summary of the available results about the thermal properties of TaC_x from the

640   literature.

641

642   Table I

Experiment	TaC-Ne	TaC-HT1	TaC-HT2
Diffraction geometry	Axial	Radial	Radial
X-ray Wavelength (Å)	0.2966	0.4847	0.4847
DAC type	Symmetric P-C	modif. Mao-Bell	modif. Mao-Bell
diamond anvil culet (μm)	300	300	300
P transmitting Medium	Ne	no	no
P calibrant	Au, ruby	Au	Au
Temperature (K)	296	673	1073
N data points	20	22	25
Max P (GPa)	43.6	33.6	38.8
Exp time (s)	20	4	4
Max membrane P (bar)	28.4	58.9	65.0
Exp duration (h)	3	5	6
Cold compr. (GPa)		2.4	2.6

643

644   Table II

Experiment	T (K)	P (GPa)	V (Å³)	stdev P + V TaC (GPa)	<Q>	PV fit	PVT fit
TaC-Ne	296	5.1±0.1	87.06±0.01	0.19	--	yes	yes
TaC-Ne	296	6.4±0.2	86.71±0.02	0.31	--	yes	yes
TaC-Ne	296	10.3±0.1	85.79±0.02	0.22	--	yes	yes
TaC-Ne	296	11.6±0.1	85.47±0.02	0.20	--	yes	yes
TaC-Ne	296	14.5±0.3	84.81±0.02	0.35	--	yes	yes
TaC-Ne	296	17.3±0.5	84.21±0.04	0.67	--	yes	yes
TaC-Ne	296	19.7±0.6	83.82±0.04	0.82	--	yes	yes
TaC-Ne	296	22.2±0.6	83.35±0.04	0.84	--	yes	yes
TaC-Ne	296	24.6±0.5	82.91±0.04	0.74	--	yes	yes
TaC-Ne	296	27.1±0.4	82.43±0.04	0.66	--	yes	yes
TaC-Ne	296	29.5±0.5	82.02±0.04	0.76	--	yes	yes
TaC-Ne	296	31.6±0.5	81.64±0.01	0.60	--	yes	yes
TaC-Ne	296	34.1±0.6	81.21±0.01	0.64	--	yes	yes
TaC-Ne	296	36.4±0.8	80.83±0.01	0.82	--	yes	yes
TaC-Ne	296	38.4±0.6	80.48±0.01	0.66	--	yes	yes
TaC-Ne	296	40.8±0.8	80.07±0.01	0.81	--	yes	yes
TaC-Ne	296	43.6±0.7	79.63±0.01	0.77	--	yes	yes
TaC-Ne	296	38.9±0.8	80.47±0.01	0.83	--	no	yes
TaC-Ne	296	32.0±0.7	81.72±0.02	0.68	--	no	yes
TaC-Ne	296	18.8±1.0	84.11±0.04	1.06	--	no	yes
TaC-Ne	296	0.0001	88.478±0.003	0.001	--	yes	yes
TaC-HT1	673±10	7.4±0.3	86.95±0.10	0.68	0.0009	no	yes
TaC-HT1	674±10	6.0±0.3	87.10±0.11	0.70	0.0010	no	no
TaC-HT1	673±10	6.8±0.3	86.89±0.09	0.64	0.0011	no	no
TaC-HT1	673±10	8.2±0.3	86.68±0.09	0.66	0.0012	no	no
TaC-HT1	673±10	9.4±0.3	86.46±0.11	0.75	0.0014	no	yes
TaC-HT1	682±10	11.0±0.3	86.17±0.10	0.72	0.0015	no	yes
TaC-HT1	673±10	12.6±0.3	85.71±0.11	0.78	0.0018	no	yes
TaC-HT1	673±10	15.3±0.4	85.13±0.10	0.81	0.0022	no	yes
TaC-HT1	673±10	17.4±0.4	84.61±0.11	0.89	0.0024	no	yes

31

TaC-HT1	671±10	20.0±0.4	83.99±0.10	0.89	0.0030	no	yes
TaC-HT1	667±10	23.6±0.4	83.39±0.11	0.97	0.0035	no	yes
TaC-HT1	672±10	26.5±0.4	82.84±0.10	0.99	0.0040	no	yes
TaC-HT1	672±10	28.4±0.5	82.42±0.11	1.07	0.0041	no	yes
TaC-HT1	673±10	30.7±0.5	81.96±0.10	1.04	0.0044	no	yes
TaC-HT1	673±10	32.2±0.5	81.52±0.10	1.10	0.0046	no	yes
TaC-HT1	673±10	33.0±0.5	81.51±0.09	1.05	0.0047	no	yes
TaC-HT1	672±10	33.6±0.5	81.54±0.11	1.16	0.0042	no	yes
TaC-HT1	674±10	24.6±0.4	83.09±0.11	1.00	0.0014	no	yes
TaC-HT2	297	1.9±0.3	87.98±0.05	0.43	0.0006	no	yes
TaC-HT2	297	1.8±0.3	87.98±0.05	0.44	0.0005	no	yes
TaC-HT2	297	2.6±0.3	87.80±0.06	0.49	0.0007	no	yes
TaC-HT2	1073±10	2.9±0.2	88.57±0.13	0.67	0.0012	no	yes
TaC-HT2	1072±10	3.0±0.2	88.47±0.12	0.63	0.0017	no	yes
TaC-HT2	1074±10	3.0±0.2	88.46±0.12	0.64	0.0016	no	yes
TaC-HT2	1073±10	2.9±0.2	88.54±0.12	0.65	0.0013	no	yes
TaC-HT2	1069±10	2.9±0.2	88.54±0.13	0.65	0.0014	no	yes
TaC-HT2	1071±10	2.8±0.2	88.58±0.12	0.61	0.0015	no	yes
TaC-HT2	1072±10	2.9±0.2	88.66±0.12	0.64	0.0015	no	yes
TaC-HT2	1073±10	3.0±0.2	88.66±0.13	0.68	0.0016	no	yes
TaC-HT2	1073±10	3.1±0.2	88.68±0.13	0.66	0.0014	no	yes
TaC-HT2	1072±10	3.2±0.2	88.66±0.11	0.61	0.0015	no	yes
TaC-HT2	1056±10	3.2±0.2	88.59±0.12	0.63	0.0018	no	yes
TaC-HT2	1075±10	3.7±0.2	88.48±0.12	0.65	0.0020	no	yes
TaC-HT2	1074±10	11.3±0.3	86.29±0.11	0.75	0.0027	no	yes
TaC-HT2	1075±10	11.4±0.3	86.23±0.11	0.76	0.0029	no	yes
TaC-HT2	1073±10	12.0±0.3	86.08±0.13	0.85	0.0030	no	yes
TaC-HT2	1074±10	13.4±0.3	85.77±0.13	0.88	0.0033	no	yes
TaC-HT2	1073±10	14.7±0.3	85.49±0.12	0.85	0.0036	no	yes
TaC-HT2	1073±10	17.9±0.4	84.75±0.12	0.92	0.0039	no	yes
TaC-HT2	1072±10	20.7±0.4	84.20±0.13	0.99	0.0040	no	yes
TaC-HT2	1073±10	23.3±0.4	83.73±0.14	1.07	0.0041	no	yes
TaC-HT2	1074±10	25.4±0.4	83.35±0.12	1.01	0.0042	no	yes

TaC-HT2	1072±10	27.5±0.4	82.95±0.14	1.15	0.0042	no	yes
TaC-HT2	1073±10	29.4±0.4	82.65±0.12	1.12	0.0043	no	yes
TaC-HT2	1075±10	31.5±0.5	82.38±0.12	1.15	0.0043	no	yes
TaC-HT2	1074±10	32.9±0.5	82.04±0.12	1.14	0.0044	no	no
TaC-HT2	1073±10	34.9±0.5	81.78±0.12	1.21	0.0046	no	no
TaC-HT2	1073±10	36.1±0.5	81.52±0.13	1.29	0.0046	no	no
TaC-HT2	1072±10	37.8±0.5	81.28±0.12	1.25	0.0048	no	no
TaC-HT2	1073±10	38.8±0.5	81.09±0.14	1.37	0.0049	no	no

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647   Table III

This study	Parameter	1σ stdev
V_0 (Å^3)	88.478	0.020
K_{T0} (GPa)	305	5
$(dK_T/dP)_{T0}$	6.1	0.5
γ_{th0}	1.2	0.1
Q	1	2
θ_0 (K)	567	10

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650 Table IV

Reference	Ref.#	Method	Composition	V_0 (Å^3)	Density (g/cm^3)	K_0 (GPa)	G (GPa)	$(dK/dP)_0$	E (GPa)	Poisson's
This study		A-XRD + R-XRD	TaC$_{0.99}$	88.478	14.448	305±5		6.1±0.5		
Brown et al. (1966)	[28]	Thin rod Ultrasound resonance	TaC$_{0.994}$	88.424	14.489	344	216		537	0.24
Bartlett & Smith (1967)	[29]	Ultrasound pulse-echo	TaC$_{0.90}$		14.65	217±7	120±25		304±64	0.27
Jun & Shaffer (1971)	[30]	Ultrasound resonance	TaC$_{0.99}$	88.359	14.496	345	216.8		537.7	
Smith & Glaser (1973)	[17]	Neutron Inelastic Scattering	TaC	88.448	14.491	283^r	194		474	0.22
Bukatov et al. (1975)	[66]	Ultrasound pulse-echo	TaC$_{0.99}$			317	227		552	0.21
Dodd et al. (2003)	[31]	Ultrasound pulse-echo	TaC$_{0.98}$		14.478	332±39	234±27	4.97±0.25	567±68	0.215
Liermann et al. (2005)	[32]	A-XRD (Al PTM)	TaC$_{0.98}$			340±5		4*		
		A-XRD (nonhydrostatic)	TaC$_{0.98}$			347±2		4*		
		A-XRD (all data)	TaC$_{0.98}$			345±9		4±0.4		
López de-la-Torre et al.(2005)	[33]	Ultrasound resonance	TaC		14.64					
		DFT (LDA)	TaC	85.533	14.985	365±4		3.6±0.2		
		DFT (GGA)	TaC	92.652	13.833	318±4	191		550	0.21
Wu et al. (2005)	[34]	DFT (LDA)	TaC	85.184	15.046	357	215		536	0.25
Shanoun et al. (2005)	[16]	DFT (LDA)	TaC	84.605	15.149	397.6	390	3.64	882	0.13
		DFT (GGA)	TaC	89.915	14.254	318.98	313	4.34	708	0.13
Isaev et al. (2007)	[13]	DFT (GGA)	TaC	89.315	14.350	324				
Lu et al. (2007)	[35]	DFT (GGA)+Debye-Grüneisen	TaC			317	162		514	0.23
Peng et al. (2009)	[36]	DFT (GGA)	TaC	94.756	13.526	311	188	4.32	470	0.248
Li et al. (2011)	[15]	DFT (LDA)	TaC	86.586	14.802	365.3	168.8		438.8	0.3
		DFT (GGA-PBE)	TaC	95.069	13.482	304.9	120.9		320.3	0.32
		DFT (RPBE)	TaC	95.194	13.464	303.1	120.6		319.5	0.32
		DFT (PW91)	TaC	95.256	13.455	302.3	117.6		312.3	0.33
Chen et al. (2013)	[37]	A-XRD	TaC nano	88.478	14.486	433±7		4*		
		DFT (LDA)	TaC	88.478	14.486	371±3	274	4.29	660	0.21
		DFT (GGA)	TaC	88.478	14.486	310±2	221	4.25	537	0.21
Liu et al. (2014)	[38]	DFT (GGA)	TaC	96.072	13.341	293.5	166.4		491.8	0.221
Sai Gautam et al. (2014)	[39]	DFT (GGA-PBE)	TaC	87.884	14.584	344	229		563	0.227
Yu etal. (2014)	[6]	DFT (GGA)	TaC	89.315	14.350	340	214		531	0.24

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652 Table V

Reference	Ref.#	Method	Composition	Density (g/cm^3)	α_0 (10^{-6}K^{-1})	C_P (JK^{-1}Mol^{-1})	θ_0 (K)	γ_{th}	V_0 (Å^3)
Houska (1964)	[20]	EXP	TaC$_{1.02}$	14.538	18				88.270
Kempter (1969)	[19]	EXP	TaC$_{0.994}$				572		
Kelley (1940)	[21]	EXP	TaC			36.66			
Elliott & Kempter (1958)	[22]	EXP	TaC$_{0.984}$	14.491	19.77				88.360
Jun & Shaffer (1971)	[23]	EXP	TaC$_{0.99}$		20.01				
Jun & Shaffer (1971)	[30]	EXP	TaC$_{0.99}$	14.496			556	1.47	88.360
Dodd et al. (2003)	[31]	EXP	TaC$_{0.98}$	14.478			593±71		
Lu et al. (2007)	[35]	COMP	TaC				808	2.34	
Peng et al. (2009)	[36]	COMP	TaC	13.526	21		541	2.08	94.760
Liu et al. (2014)	[38]	COMP	TaC	13.341			509.4		96.07
Sai Gautam et al. (2014)	[39]	COMP	TaC	14.584		38.93	588.3		87.883
Frisk & Guillermet (1996)	[24]	COMP	TaC			36.61	551		

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TaC$_{0.99}$ at 29.4 GPa, 1073 K