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Spinel-type Al_4C_3 attainable above 7 GPa and more high-pressure phases of Al_4C_3

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We predict that Al_4C_3 adopts a cubic, anti-spinel-type structure (Al_4C_3-II) between 7 and 33 GPa, peaking in stability relative to other Al_4C_3 structures at 26 GPa. At ambient pressure, Al_4C_3-II is mechanically robust, with a bulk modulus of 160 GPa and a Vickers hardness of around 30 GPa. Beyond Al_4C_3-II, we identify three additional post-spinel phases appearing in the Al_4C_3 phase diagram, including an anti-Th_3P_4-type at 140 GPa. The clear enthalpy differences under pressure leave little doubt that the known trigonal $R\bar{3}m$ ground state of Al_4C_3 will undergo multiple phase transitions. The accessible pressure window for spinel-type Al_4C_3-II is easily accessible in both laser-heated diamond anvil cell and large-volume multi-anvil cell experiments. We therefore encourage experimental exploration of the Al–C system at high pressure.

Introduction

High-pressure chemistry is a rich field in materials research, and advanced synthesis techniques have delivered a variety of new compounds in recent times.[1–4] A notable research method is the laser heating-diamond anvil cell (LH-DAC) used in conjunction with *in situ* X-ray diffraction (XRD).[5–7] Modern LH-DAC equipment can explore temperatures and pressures above ~5000 K and 300 GPa,[8–10] and enables dynamic compression rates of several 100 GPa s^{-1}.[11–13] Larger volumes of material can be synthesized using Multi-Anvil-Cells (MAC) at pressures up to 50 GPa.[14]

Computational methods are now a standard tool for characterizing synthesized materials and are essential for exploring the phase space and advancing experimental research at high pressure.[15,16] For example, the spinel-type γ-Si_3N_4 was achieved at 15 GPa and 2000 K through a collaborative effort of computation and experiment.[17] Recently, after more than three decades of effort, a crystal phase of C_3N_4 was synthesized at high pressure (>100 GPa).[18–21]

Hitherto, the only known polymorph of Al_4C_3 is the trigonal ($R\bar{3}m$) ground state structure.[22–24] The high-pressure behavior of Al_4C_3 was explored up to 6 GPa at 300 K.[25] Exploration at higher temperatures occurred only up to 8 GPa, but resulted in an incongruent thermal decomposition of Al_4C_3.[26,27] Recently, M_4C_3 with anti-Th_3P_4 type structures have been synthesized for Dy_4C_3 at 19 GPa and for Sc_4C_3 at 10 GPa.[28,29] Despite its simplicity, Al_4C_3 appears to have been overlooked,[30,31] and our own efforts had been communicated but not published. However, its composition suggests it may display a similar rich high-pressure chemistry as Si_3N_4.[32–38]

Results and discussion

While computing several hundred polymorphs with composition A_4X_3 at different pressures, we ultimately identified four high-pressure modifications of Al_4C_3, indexed with Roman numerals (II, III, IV, and V), that surpass the trigonal ground-state modification Al_4C_3-I. In sequence, these are an anti-spinel type, an anti-$CaFe_2O_4$-like orthorhombic modification, an anti-$CaFe_2O_4$-type, and an anti-Th_3P_4 type. Polyhedral structure depictions are shown in Fig. 1.

Ground state energies, lattice parameters, volumes, and bulk moduli of the structures are given in Table 1. The energy–volume, ΔE–V, diagram is shown in Fig. 2a, the corresponding pressure–volume diagram in Fig. 2b, and the enthalpy–pressure, ΔH–p, diagram is presented in Fig. 2c. Accordingly, the ground state modification will transform into the denser (anti-) spinel type of Al_4C_3-II at 7 GPa. This is a relatively low-pressure process that can be attained with various experimental equipment, including large-volume presses. The largest enthalpy difference of Al_4C_3-II to another phase, hence the maximum driving force for its formation, about 0.2 eV/Al_4C_3, is attained at 26 GPa. At 33 GPa, cubic Al_4C_3-II will be superseded by an orthorhombic structure that is related to the (anti-) $CaFe_2O_4$-type. This Al_4C_3-III remains favored up to 50 GPa, at which point it will transform into an

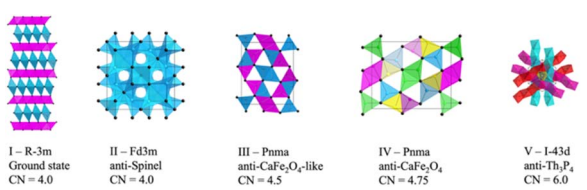

Fig. 1 The five phases of Al_4C_3 studied. Space groups and (average) coordination numbers (CN) of Al are indicated. Black spheres represent carbon; aluminum is depicted in colored polyhedra.

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Table 1 Energy, lattice parameters, and volume of Al_4C_3 structures. The bulk modulus B_0 is computed from $E-V$ data using the Murnaghan equation of state

	Energy (eV/Al_4C_3)	Lattice parameters (Å)	Volume (Å^3/Al_4C_3)	Bulk modulus (GPa)
I	−62.89	$a = 3.33$ $c = 24.88$	79.64	172
II	−62.81	$a = 8.53$	77.65	176
III	−61.83	$a = 9.24$ $b = 3.12$ $c = 10.08$	72.56	170
IV	−61.02	$a = 8.79$ $b = 3.03$ $c = 10.45$	69.61	171
V	−59.56	$a = 6.48$	68.00	—

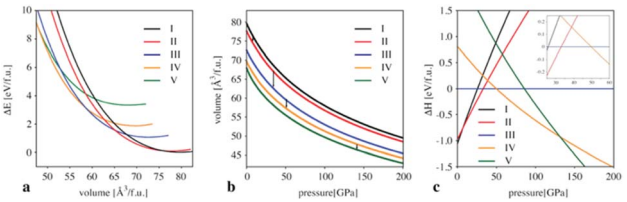

Fig. 2 (a) Energy–volume, $\Delta E-V$, diagram of relevant Al_4C_3 polymorphs. The energy is given relative to Al_4C_3-I. (b) Pressure–volume diagram of relevant Al_4C_3 polymorphs. The arrows indicate transition pressures between the phases. Note that Al_4C_3-V is mechanically unstable below 30 GPa. (c) Enthalpy–volume, $\Delta H-p$, diagram of relevant Al_4C_3 polymorphs. The enthalpy is given relative to Al_4C_3-III. The insert in the upper right corner details the transition sequence II–III–IV between 25 and 60 GPa. Black, red, blue, orange, and green lines represent Al_4C_3-I, II, III, IV, and V, respectively.

(anti-) $CaFe_2O_4$-type. Finally, at pressures above 140 GPa, an (anti-) Th_3P_4-type of Al_4C_3-V will be the most favorable structure. This final structure resembles the high-pressure phases of Sc_4C_3 and Dy_4C_3, attained at 10 and 19 GPa, respectively.[28,29] Hence, the larger trivalent cations of Sc and Dy attain the (anti-) Th_3P_4-type at much lower pressures than the smaller Al^{3+} – a trend commonly observed in high-pressure chemistry of elements and compounds, including sesquioxides and sesquisulfide.[39–41] As expected, the densities of the Al_4C_3 polymorphs increase from phase I to V. Since the bulk moduli of the polymorphs are comparable, the initial slopes of the pressure–volume graphs (Fig. 2b) are very similar. That they remain so indicates a similar pressure dependence of the compressibility of the polymorphs. The average coordination number of Al_4C_3 polymorphs increases from phase I to V—except for the transition from the ground-state to the spinel-type structure (Fig. 1). This progression of phases thus reflects a systematic densification and coordination enhancement under pressure. The sequence of phase transformations, including transition pressure p_t and volume change at p_t, is summarized by

$$\mathrm{I} \xrightarrow[-2.5\%]{7\ \mathrm{GPa}} \mathrm{II} \xrightarrow[-6.6\%]{33\ \mathrm{GPa}} \mathrm{III} \xrightarrow[-3.8\%]{50\ \mathrm{GPa}} \mathrm{IV} \xrightarrow[-3.0\%]{140\ \mathrm{GPa}} \mathrm{V}$$

At ambient pressure, the energy difference between the (anti-) spinel-type of Al_4C_3-II and the ground state modification Al_4C_3-I is only 80 meV/Al_4C_3. LDA calculations even place Al_4C_3-II below Al_4C_3-I by 23 meV/Al_4C_3, although both structures are built up by AlC_4-tetrahedra only, and, thus, the number of nearest atoms (coordination number) of Al is identical.

Table 2 Elastic constants (GPa) of Al_4C_3 polymorphs (I–V) computed at zero pressure (0 GPa)

	I	II	III	IV	V
C_{11}	347	342	306	351	110
C_{22}	347	342	424	510	110
C_{33}	397	342	455	407	110
C_{44}	111	168	17	65	−966
C_{55}	116	168	17	53	−966
C_{66}	116	168	151	141	−966
C_{12}	124	94	65	76	134
C_{13}	55	94	78	44	134
C_{14}	14	0	0	0	0
C_{23}	55	94	47	44	134

The elastic constants of Al_4C_3 polymorphs (I–V) computed at zero pressure are shown in Table 2. Based on stability criteria,[42,43] the structures of Al_4C_3-I–IV are mechanically stable at ambient pressure. Thus, the high-pressure phases may be recoverable. While Al_4C_3-V is mechanically stable at 140 GPa, it becomes unstable below ∼30 GPa. A possible distortion along a Bain strain path may transform it into the spinel-type Al_4C_3-II.[33] The elastic constants can be used to compute the aggregate moduli, particularly the elastic shear modulus G. We obtain 123, 148, 70, and 110, for Al_4C_3-I–IV, respectively. Using the formula of Chen,[44] we estimate the Vickers hardness of Al_4C_3-I to 22 GPa and that of spinel-type Al_4C_3-II to 30 GPa. All polymorphs of Al_4C_3 presented here are semi-conductors, with band gaps of 1.6, 1.4, 1.9, 2.2, and 2.5 eV (GGA values) for Al_4C_3-I–V, respectively.

Computational method

We started our search for potential high-pressure modifications of Al_4C_3 by screening models that we previously considered for Si_3N_4.[45] The results were confirmed by evolutionary algorithms using the USPEX code,[46–48] with a slight modification to Al_4C_3-III. All structures were computed using density functional theory (DFT), implemented with the Vienna *Ab initio*

Simulations Package (VASP).[49,50] We employed the projector augmented wave (PAW) formalism, along with the strongly constrained and approximately normed (SCAN) functional, for electron correlation and exchange.[51–53] A plane wave energy cutoff of 500 eV was applied, and fine grids sampled the Brillouin zone with spacings of 0.030–0.040 $Å^{-1}$.[54] With these parameters, forces, and energies converged to within 5 meV $Å^{-1}$ and 0.1 meV per atom, respectively. Throughout the work, we approximate Gibbs energy differences by enthalpy differences, hence $\Delta G \approx \Delta H$. Potential contributions from defects, non-stoichiometry, or surface effects during growth may be factors that alter the thermodynamic balance through configurational or vibrational entropy. We assume that if these effects occur, they affect all structures similarly. Remaining entropy differences are, in general, much smaller in comparison to the much larger variation of ΔH within a few GPa of pressure. Justification for this common approach stems from calculations of the phase boundary between the β- and γ-phase of Si_3N_4, with γ-Si_3N_4 adopting the spinel-structure,[55] and from the prediction of a synthesis of Hf_3N_4 with Th_3P_4-structure from the elements.[56]

Conclusions

We predict a cubic (anti-) spinel-type of Al_4C_3 succeeding the known trigonal ground state modification at higher pressures. While Al_4C_3-II is 0.08 meV/Al_4C_3 above the ground state at ambient pressure, it becomes thermodynamically favored between 7 and 33 GPa with a maximum enthalpy difference (hence, driving force) of 0.2 eV $f.u.^{-1}$ at 26 GPa. Al_4C_3-II is also stable against decomposition into the elements, by 1.8 and 1.7 eV/Al_4C_3 at ambient pressure and 30 GPa, respectively. The reported energy differences are well above the "uncertainty" of DFT calculations for enthalpies of formation differences, about 10 meV per atom.[57] The proposed stability range of spinel-type Al_4C_3 is accessible with large-volume presses[58] or LH-DAC.[5] However, high temperatures may be required to facilitate the transition. Previous experiments examined pressures up to 8 GPa and maintained temperatures below 2500 K.[26,27] Al_4C_3-II is mechanically stable at ambient pressure, with a bulk modulus of 160 GPa comparable to that of Fe_3C or ThC.[59,60] The hardness of Al_4C_3-II will be substantially higher than that of the known modification, we estimate $H_v \approx 30$ GPa for Al_4C_3-II.

Beyond Al_4C_3-II, the phase diagram of Al_4C_3 features three post-spinel modifications. Several other materials also exhibit post-spinel modifications, including $CaFe_2O_4$, $ZnGa_2O_4$, and $CdCr_2Se_4$.[61–66] For Si_3N_4, such phases were also proposed,[45,61] but ultimately a pernitride SiN_2 with N_2^{4-}-units emerged. Motivated by this analogy, we explored a series of Al–C compounds with C_2-dimers in various oxidation states (C_2^{2-}, C_2^{4-}, and C_2^{6-}), but none yielded a thermodynamically stable polymorph. In addition to Al_4C_3-I to Al_4C_3-V, we also identified several candidate structures of Al_4C_3 that, at certain pressures, approach the stability of the thermodynamically most favorable structure shown here. These include types related to $SrPb_2O_4$, P_4S_3, and further variants of the $CaFe_2O_4$-type. While our calculations neglect possible contributions from defects, non-stoichiometry, or surface effects – factors that could alter the thermodynamic balance through configurational or vibrational entropy – it is evident that Al_4C_3 will undergo pressure-induced phase transitions. We therefore encourage experimental efforts to synthesize the predicted Al_4C_3-II modification and advance the high-pressure chemistry of metal carbides.

Author contributions

Mitchell Falgoust: writing – review & editing, writing – original draft, visualization, methodology, investigation, formal analysis, data curation. Peter Kroll: writing – review & editing, writing – original draft, visualization, supervision, resources, project administration, methodology, investigation, funding acquisition, formal analysis, data curation, conceptualization.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the article is available from the corresponding author upon reasonable request.

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