Discovery of carbon-vacancy ordering in Nb$_4$AlC$_{3-x}$ under the guidance of first-principles calculations

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The conventional wisdom to tailor the properties of binary transition metal carbides by order-disorder phase transformation has been inapplicable for the machinable ternary carbides (MTCs) due to the absence of ordered phase in bulk sample. Here, the presence of an ordered phase with structural carbon vacancies in Nb$_4$AlC$_{3-x}$ ($x \approx 0.3$) ternary carbide is predicted by first-principles calculations, and experimentally identified for the first time by transmission electron microscopy and micro-Raman spectroscopy. Consistent with the first-principles prediction, the ordered phase, o-Nb$_4$AlC$_3$, crystalizes in $P\overline{6}_3/mcm$ with $a = 5.423\,\text{Å}$, $c = 24.146\,\text{Å}$. Coexistence of ordered (o-Nb$_4$AlC$_3$) and disordered (Nb$_4$AlC$_{3-x}$) phase brings about abundant domains with irregular shape in the bulk sample. Both heating and electron irradiation can induce the transformation from o-Nb$_4$AlC$_3$ to Nb$_4$AlC$_{3-x}$. Our findings may offer substantial insights into the roles of carbon vacancies in the structure stability and order-disorder phase transformation in MTCs.

Machinable ternary carbides (MTCs, having a general chemical formula $M_mA_nC_{m-n}$, where M is an early transition metal element; A is an A group element; $m$ and $n$ are integers, $m \geq 2$) are the most investigated carbides in the last two decades. Crystallizing in the $P\overline{6}_3/mcm$ (for $n = 1$)$^{6,10}$ or $R\overline{3}m$ (for $n = 2$)$^{10,11}$ space group, their crystal structures are closely related, which can be regarded as the periodically stacking of strongly bonded “M$_m$C$_{m-n}$” sheets and “A” atomic layers along [0001]. The building block of “M$_m$C$_{m-n}$” in the MTCs strongly resembles that in the binary carbides. The presence of structural carbon vacancies in the MTCs are widely postulated$^{12}$ since monolithic MTCs can be synthesized only with certain degree of carbon deficiency$^{13}$. The carbon vacancies have been believed to be disordered before the pioneering work by Etzkorn and coworkers$^{14}$ on V$_4$AlC$_{3-x}$ single crystal (with a dimension of $0.2 \times 0.2 \times 0.01\,\text{mm}$) grown by the auxiliary metal bath technique. They pointed out that the V$_4$AlC$_{3-x}$ single crystal grown at 1500°C holds 10% disordered carbon vacancies, while the carbon vacancies become ordered at 1300°C, forming V$_{12}$Al$_4$C$_8$. So far, the knowledge of the carbon vacancies in the interesting MTCs is quite limited$^{12}$.

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First-principles calculation is a powerful tool to investigate the point defects, crystal structure and properties of the MTCs\textsuperscript{7,15–19}. However, it is frustrating for the phase stability of stoichiometric Nb\textsubscript{4}AlC\textsubscript{3}. Theoretically, Wang et al.\textsuperscript{20} argued that stoichiometric Nb\textsubscript{4}AlC\textsubscript{3} is unstable and decomposes to Nb\textsubscript{2}AlC and NbC above 57 K. Experimentally, Hu et al.\textsuperscript{21} demonstrated that Nb\textsubscript{4}AlC\textsubscript{3} has a good stability at 2000 K. Since Nb\textsubscript{4}AlC\textsubscript{3} bears striking resemblance to V\textsubscript{4}AlC\textsubscript{3}, this puzzling and unsolved inconsistence necessitates the revisiting of the crystal structure of Nb\textsubscript{4}AlC\textsubscript{3} with considerations of carbon vacancies.

Here, under the guidance of the first-principles prediction, an ordered phase bearing structural carbon vacancies in Nb\textsubscript{4}AlC\textsubscript{3−\textit{x}} (\textit{x} ≈ 0.3), \textit{o}-Nb\textsubscript{12}Al\textsubscript{3}C\textsubscript{8}, is unambiguously identified in experiment, demonstrating the validity to investigate the carbon vacancies in the MTCs with the combination of first-principles calculations, electron diffractometry and Raman spectroscopy.

Results

Predication of ordered phase. In analogy with the carbon-vacancy ordered phase in V\textsubscript{4}AlC\textsubscript{3−\textit{x}} (Ref. 14), ten hypothetical carbon-vacancy configurations (VCs) with a vacancy concentration of 1/9 were constructed based on a $\sqrt{3} \times \sqrt{3}$ supercell of Nb\textsubscript{4}AlC\textsubscript{3} (Fig. 1a–j). There are two distinct types of Nb\textsubscript{6}C octahedrons in Nb\textsubscript{4}AlC\textsubscript{3} (P\textsubscript{6}\textsubscript{3}/mmc), involving the carbon atoms located at 4\textit{f} sites with a Nb–C bond length of 2.21 Å (OCT-4\textit{f}) and 2\textit{a} sites with a Nb–C bond length of 2.28 Å (OCT-2\textit{a}). VC1, VC8 and VC10 have two OCT-2\textit{a} type carbon-vacant octahedrons in each unit cell. In contrast, VC3, VC4, VC5, VC6 and VC7 have two OCT-4\textit{f} type carbon-vacant octahedrons. VC2 and VC9 own one OCT-2\textit{a} and one OCT-4\textit{f} type carbon-vacant octahedrons. The crystal structure information of the constructed VCs is provided in Supplementary Table 1. To evaluate the phase stability, the formation energy for VC ($E_{\text{fVC}}$) is calculated by $E_{\text{fVC}} = E_{\text{VC}} - 3E_{\text{Nb}\textsubscript{4}\text{AlC}\textsubscript{3}} + 2\mu_{\text{C}} - E_{\text{VC}}$ and $E_{\text{Nb}\textsubscript{4}\text{AlC}\textsubscript{3}}$ are total energies of the VC and Nb\textsubscript{4}AlC\textsubscript{3} unit cell, respectively. The chemical potential of carbon, $\mu_{\text{C}}$, is assumed to be that in graphite. Table 1 lists the calculated values. With lower total energies, VC8 and VC10 are the energetically most possible VCs. The $E_{\text{fVC}}$ for VC8 and VC10 are negative (a brief discussion in the context of chemical potential is provided in Supplementary Note 1), indicating that stoichiometric Nb\textsubscript{4}AlC\textsubscript{3} is metastable and prone to spontaneously forming ordered phases. With a more negative $E_{\text{fVC}}$, VC8 isostructural with
V₁₂Al₃C₄ (Ref. 14) is slightly more favorable than VC10 from an energetic point of view. The mechanical stability of crystals requires the elastic constants $c_{ij}$ to match the Born–Huang criterion. Specifically, the restrictions for hexagonal crystal system are: $c_{11} + c_{12} > 2\frac{c_{44}}{c_{11}}$, $c_{44} > 0$, $c_{66} = \frac{c_{11} - 2c_{12}}{2} > 0$. According to the calculated elastic constants in Supplementary Table 2, VC8 and VC10 satisfy the mechanical stability criteria. In addition, the phonon dispersion curves in Supplementary Fig. 1 have no imaginary frequencies. VC8 and VC10 are therefore dynamically stable.

Identification of ordered phase and determination of crystal structure. To test the theoretical prediction, the phase component of the as-prepared Nb₄AlC₃–δ (x ≈ 0.3) was revisited. Like other MTCs, grains of Nb₄AlC₃–δ are elongated with ca. 54 μm in length and 10 μm in width, as shown in Fig. 2a. Indexing the low-index zone axis electron diffraction patterns (EDPs) in Fig. 2b–d results in a new hexagonal structure with $a = 5.5$ Å, $c = 25.2$ Å, which is different from that of previously reported Nb₄AlC₃ ($a = 3.1$ Å, $c = 24.1$ Å)²⁴. For convenience, the new phase is denoted as o-Nb₄AlC₃. Then, Fig. 2b–d correspond to the EDP of [0001], [1210] and [0110] of o-Nb₄AlC₃, respectively. The reflection conditions $l = 2n$ for (hh0) and (000). The appearance of (000) with $l = 2n + 1$ in Fig. 2d is caused by double diffractions, which can be verified by its disappearance in the EDP collected along [hkl0] (Fig. 2e). The convergent beam electron diffraction (CBED) patterns with different convergence angles along [0001] in Fig. 2f,g demonstrate that there is a six-fold rotation axis and two mirror planes along [0001]. In addition, the CBED pattern collected along [hkl0] in Fig. 2h indicates a mirror plane vertical to [0001]. Therefore, the corresponding point group is 6/mmm. Considering the reflection conditions, the space group of o-Nb₄AlC₃ is determined to be P6₃/mcm. Noteworthily, the diffraction spots marked by black arrows in Fig. 2b–d can be indexed with Nb₄AlC₃–δ as well. Figure 3a,b present transmission electron microscopy (TEM) dark field morphologies imaged with [101] and [303] of o-Nb₄AlC₃, respectively. Since (303) of o-Nb₄AlC₃ coincides with (1120) of Nb₄AlC₃–δ (Fig. 2b,c), the dark domains with irregular shape in Fig. 3a are Nb₂AlC₃–δ, while the regions with bright contrasts correspond to o-Nb₄AlC₃. The worm-like ribbons marked by arrows are antiphase boundaries in o-Nb₄AlC₃.

As determined by electron-probe X-ray microanalysis, the molar ratio of Nb:Al in o-Nb₄AlC₃ is 4:1.05 (see Supplementary Table 3). The energy dispersive X-ray spectroscopy (EDS) mapping of Al (Fig. 3c) and Nb (Fig. 3d) demonstrates that there is no compositional difference of Al and Nb between o-Nb₄AlC₃ and Nb₄AlC₃–δ. In addition, carbon is 10% deficient in the starting materials to synthesize monolithic Nb₄AlC₃–δ. Then, the chemical formula of o-Nb₄AlC₃ is Nb₂Al₁⁺₈C₁₈₋₄n³ (δ = 0.3) since the unit cell of o-Nb₄AlC₃ is three times that of Nb₄AlC₃–δ (Fig. 4a). As the lowest multiplicity for the Wyckoff sites of P6₃/mcm (Ref. 25) is 2, the formation of o-Nb₄AlC₃ cannot be caused by an excess of Al, otherwise the minimum Al/Nb is 8/24 with δ = 2. Considering the nominal composition of the starting materials (Nb:C = 12.8:1) and restrictions on the Wyckoff sites of P6₃/mcm (Ref. 25), o-Nb₄AlC₃ is Nb₂AlC₃ with the carbon vacancies occupying the 2b Wyckoff site. Namely, o-Nb₄AlC₃ has the VC8 configuration. The experimental EDPs and simulated patterns with the VC8 configuration are in excellent consistence (see Supplementary Fig. 2a–f). The crystal structure information of o-Nb₄AlC₃ is listed in Table 2. o-Nb₄AlC₃ can be constructed readily by removing the carbon atoms at (0, 0, 0) and (0, 0, 1/2) of the $\sqrt{3} \times \sqrt{3}$ supercell (Fig. 4b). The orientation relationship is: [1210] o-Nb₄AlC₃ || [1100] Nb₄AlC₃–δ, [0010] o-Nb₄AlC₃ || [1210] Nb₂AlC₃–δ.

**Table 1. Total energy and formation energy for various VCs.** Formation energy for VC. The total energy of Nb₄AlC₃ unit cell and chemical potential of carbon in graphite is −2191.204 and −154.990 eV, respectively.

| Configuration | Total energy (eV) | $E_{f\text{c}}^\text{VC}$ (eV) |
|---------------|------------------|------------------------------|
| VC1           | -6262.961        | 0.671                        |
| VC2           | -6262.534        | 1.098                        |
| VC3           | -6261.248        | 2.384                        |
| VC4           | -6261.351        | 2.019                        |
| VC5           | -6261.332        | 2.280                        |
| VC6           | -6261.464        | 2.168                        |
| VC7           | -6261.864        | 1.768                        |
| VC8           | -6264.590        | -0.958                       |
| VC9           | -6264.974        | 0.658                        |
| VC10          | -6264.516        | -0.884                       |

Raman spectroscopic verification of o-Nb₄AlC₃. To further verify the crystal structure, micro-Raman spectroscopic investigations were conducted. The polarized and unpolarized Raman
spectra are presented in Fig. 4c–e. The group theory predicts the following symmetries for zone-center (Γ point) optical phonons: \( \Gamma_{\text{optical}} = 7A_{1g} + 3A_{1u} + 5A_{2g} + 7A_{2u} + 4B_{1g} + 8B_{1u} + 7B_{2g} + 4B_{2u} + 11E_{1g} + 12E_{2g} + 11E_{1u} + 11E_{2u} \), where \( A_{1g} \), \( E_{1g} \) and \( E_{2g} \) are Raman active modes. The experimental and theoretical Raman shifts calculated by first-principles (Table 3) are well consistent. In addition, the peaks located at 158 (\( \omega_{158} \)), 169 (\( \omega_{169} \)), 220 (\( \omega_{220} \)), 259 (\( \omega_{259} \)), 287 (\( \omega_{287} \)), 616 (\( \omega_{616} \)) and 681 cm\(^{-1}\) (\( \omega_{681} \)) disappear in the polarized Raman spectrum, indicating a symmetry of \( A_{1g} \) (Ref. 11), which is exactly the same with that predicted by the first-principles calculations. Therefore, the Raman spectroscopic investigation unambiguously validates the crystal structure of o-Nb\(_4\)AlC\(_3\) with the predicted VC8 configuration.

Figure 2. Grain morphology and EDPs. (a) Scanning electron microscopy image of the as-prepared Nb\(_4\)AlC\(_3-x\). Inset is an electron backscatter diffraction image. The grains are elongated. Selected area EDPs belonging to (b) [0001], (c) [1210], (d) [0110] and (e) [hk0] of o-Nb\(_4\)AlC\(_3\) are indexed in red fonts. The diffraction spots marked by black arrows coincide with those of Nb\(_4\)AlC\(_3-x\), as denoted with black indices. CBED patterns were collected along (f,g) [0001] and (h) [hk0]. (f) and (g) were recorded with different convergence angles. A (0000) CBED disk was montaged in (h). “m” and “c*” stand for mirror plane and [0001] direction in reciprocal space, respectively.

Figure 3. Coexistence of o-Nb\(_4\)AlC\(_3\) and Nb\(_4\)AlC\(_3-x\) and composition analysis. TEM dark field images were recorded with (a) (1010) and (b) (3030) of o-Nb\(_4\)AlC\(_3\). EDS mapping in the squared region in (a) with (c) Al and (d) Nb.
Figure 4. Crystal structure and Raman spectrum of o-Nb₄AlC₃. (a) Illustration of the unit-cell projection of o-Nb₄AlC₃ (red) and Nb₄AlC₃₋ₓ (black) along [0001]. The EDPs in Fig. 2c,d demonstrate that the lengths of c axis of o-Nb₄AlC₃ and Nb₄AlC₃₋ₓ in the present experiment are identical. (b) Unit cell of o-Nb₄AlC₃ (left) and the projection of edge-sharing Nb₆C octahedrons along [001] (median) and [101] (right). The octahedral interstitial sites at the origin and (0, 0, 1/2) are not occupied by carbon atoms. The blue, red and purple balls illustrate the Nb, Al and C atoms. (c) Polarized and unpolarized Raman spectrums collected with a 600 lines per mm diffraction grating. (d,e) Unpolarized Raman spectrums collected with a 1800 lines per mm diffraction grating in the wavenumber ranges boxed in (c).

Table 2. Crystal structure information of o-Nb₄AlC₃. The values determined by electron diffraction and XRD are \( a = 5.5 \text{ Å}, c = 25.2 \text{ Å} \) and \( a = 5.423 \text{ Å}, c = 24.146 \text{ Å} \), respectively.
Therefore, o-Nb₄AlC₃ is a low-temperature phase; while Nb₄AlC₃ becomes disordered. With weaker Nb–C bonds, forming a carbon vacancy gives rise to carbon-vacancy ordered phases²⁶,²⁷. With weaker Nb–C bonds, forming a carbon vacancy and stabilizes the structure. The triumph of the stabilizing factor over the destabilizing one dilatation of the carbon-vacant octahedron strengthens the remaining Nb–C bonds around the carbon structure. Meanwhile, the redistribution of the electron charge within the vacancy neighbors through the Table 3. Experimental and theoretical Raman shifts of o-Nb₄AlC₃. The theoretical Raman shifts and symmetry information are provided in the parentheses. Recorded with a diffraction grating of 1800 lines per mm.

Statistics on the TEM dark field morphologies imaged with superlattice diffraction spots indicate that o-Nb₄AlC₃ accounts for ca. 81 vol.% of the as-prepared sample. The X-ray diffraction (XRD) pattern in Fig. 5a is indexed with o-Nb₄AlC₃. The superlattice peaks, (h0hI) with h = 5n ± 1, are unidentifiable in the XRD pattern due to their remarkably low intensities (see Supplementary Table 4).

Discussion
Formation of a carbon vacancy within the Nb₄C octahedron breaks six Nb–C bonds and destabilizes the structure. Meanwhile, the redistribution of the electron charge within the vacancy neighbors through the dilatation of the carbon-vacant octahedron strengthens the remaining Nb–C bonds around the carbon vacancy and stabilizes the structure. The triumph of the stabilizing factor over the destabilizing one gives rise to carbon-vacancy ordered phases²⁶,²⁷. With weaker Nb–C bonds, forming a carbon vacancy in OCT-2α costs less energy than that in OCT-4f (Fig. 5b). Similar features have been confirmed in Ta₄AlC₃ and Ti₄AlN₃ (Ref. 16,17). Generally speaking, the more the diagonal distances of the Nb atoms in the carbon-vacant octahedron expand, the stronger the remaining Nb–C bonds around the carbon vacancy become, and then the more stable the carbon-vacant structure is (Fig. 5b). Therefore, VC₈ and VC₁₀ with carbon vacancies only in OCT-2α and most expansions of the carbon-vacant octahedrons have lower total energies than the other VCs.

The revisiting of the phase component in Nb₄AlC₃₋ₓ confirms the presence of carbon-vacancy ordered phase predicted by our first-principles calculations: o-Nb₄AlC₃ has the VC₈ configuration. The difference of $E_{VC}^f$ between VC₁₀ and VC₈ is only 0.07 eV, and it is therefore not unreasonable to anticipate the existence of VC₁₀. Virtually, there are several weak Raman peaks belonging to neither o-Nb₄AlC₃ (VC₈) nor Nb₄AlC₃₋ₓ in the Raman spectrum collected with a 1800 lines per mm diffraction grating (Fig. 5c). These extra peaks are most likely generated by VC₁₀ (see Supplementary Table 5). Since no EDPs belonging to VC₁₀ (see Supplementary Fig. 2g–i) were identified in the present study, VC₁₀ is believed to exist not in a highly ordered manner. The crystal structure information of VC₁₀ is provided in Supplementary Table 6.

Carbon-vacancy ordered phase is stable at low temperature¹. When temperature rises and the contribution of entropy to the Gibbs free energy is appreciable, carbon vacancies tend to be in short-range order or disordered. Therefore, o-Nb₄AlC₃ is a low-temperature phase; while Nb₄AlC₃₋ₓ (with certain amounts of disordered carbon vacancies) is the corresponding high-temperature phase. As indicated by the first-principles calculations (Table 1, Fig. 5b) and Rietveld refinements of X-ray (neutron) diffraction patterns of V₄AlC₃₋ₓ (Ti₄AlN₃₋ₓ)¹⁴,²⁸, the disordered vacancies in Nb₄AlC₃₋ₓ are most likely located at the 2a site of the P6₃/mmc space group. The existence of carbon-vacancy disordered Nb₄AlC₃₋ₓ at room temperature is due to the fact that the cooling rate during the sample synthesis is not slow enough, and brings about disordered domains (Figs 3a and 6a). When o-Nb₄AlC₃ is heated above a critical temperature, transformation to Nb₄AlC₃₋ₓ occurs with the nucleation and growth of new disordered nanodomains in the ordered phase (Fig. 6b). For the sample quasi-quenched from 1400°C after keeping...
30 min, the amount of disordered domains (with dark contrasts) increases from ca. 19 vol.% (Fig. 6a) to 36 vol.% (Fig. 6b). Dwelling for 10 s at 1500 °C, nearly all o-Nb₄AlC₃ transforms to Nb₄AlC₃–ₓ, leaving some ordered nanodomains (with bright contrasts, Fig. 6c). Consequently, the EDP (Fig. 6d) exhibits the

Figure 5. XRD pattern, dilatation of the carbon-vacant octahedron and extra Raman peaks. (a) XRD pattern of the as-prepared Nb₄AlCₓ. All identifiable peaks belonging to o-Nb₄AlC₃ and Nb₄AlC₃–ₓ coincide. For the sake of conciseness, they are indexed with the cell of o-Nb₄AlC₃. (b) Change of diagonal distances of Nb (blue balls in the inset) in the carbon-vacant octahedron using the values of Nb₆C octahedrons as references. Red balls and stars denote the octahedrons with a carbon vacancy located at the 2a and 4f sites of Nb₄AlC₃–ₓ (P6₃/mmc), respectively. (c) Raman spectrum collected with a 1800 lines per mm diffraction grating. Arrows denote the extra weak Raman peaks not belonging to o-Nb₄AlC₃ or Nb₄AlC₃–ₓ. Those peaks are believed to be generated by the vibration of VC10.

Figure 6. Domain morphologies and electron irradiation. TEM dark field image recorded with (1010) of o-Nb₄AlC₃ in the sample (a) as-prepared, (b) quasi-quenched from 1400 °C after dwelling for 30 min, and (c) quasi-quenched from 1500 °C after dwelling for 10 s. o-Nb₄AlC₃ and Nb₄AlC₃–ₓ are in bright and dark contrasts, respectively. Inset in (b) is an enlarged morphology demonstrating the disordered nanodomains. (d) An EDP with the features of short-range ordering. The superlattice diffraction spots become weak streaks. (e) Dependence of Iₛ/IS₁ on the irradiation time. IS₁ and IS₂ are the intensities of the diffraction spots marked in the inset. (f,g) EDPs recorded after irradiated 120 s. (f,g) belong to [0001] and [1100] of Nb₄AlC₃–ₓ, respectively. The electron dose for irradiation is approximately 0.04 e Å⁻² s⁻¹.
features of short-range ordering. Thereby, similar to the carbon-vacancy disordering in V₄AlC₄₋ₓ where the disordering occurs in the range from 1300°C to 1500°C, that in Nb₄AlC₃₋ₓ starts around 1400°C and completes at 1500°C.

Resembling the ordered phase in binary carbides, transformation from o-Nb₄AlC₃ to Nb₄AlC₃₋ₓ can be induced by electron irradiation, as shown in Supplementary Movies 1,2. The intensity of the superlattice diffraction spots decreases dramatically as the irradiation proceeds (Fig. 6e). Irradiated for approximately 120 s, the superlattice diffraction spots disappear (Fig. 6f,g) with the transformation from o-Nb₄AlC₃ to Nb₄AlC₃₋ₓ. The extremely electron irradiation sensitive nature possibly hides o-Nb₄AlC₃ and domains from being discovered before.

In summary, under the guidance of first-principles calculations, a new carbon-vacancy ordered phase, o-Nb₄AlC₁₋ₓ (Nb₄₋ₓAlₓC₃) has been discovered. It crystallizes in the space group of P6₃/mcm with \( a = 5.423 \text{ Å}, \ c = 24.146 \text{ Å}. \) Coexistence of ordered (o-Nb₄AlC₃) and disordered (Nb₄₋ₓAlₓC₃) phase brings about domains with irregular shape. Both heating and electron irradiation can induce the transformation from o-Nb₄AlC₃ to Nb₄₋ₓAlₓC₃. The excellent consistency between the first-principles prediction and experimental results demonstrated in this work may inspire the theoretical investigation on the vacancies in over 70 machinable ternary carbides/nitrides. The unveiled domain structure likely ignites investigation enthusiasm on the order-disorder phase transformation as well.

**Methods**

**First-principles calculations with CASTEP module.** Electronic exchange-correlation energy was treated under the generalized gradient approximation (GGA–PBE). Interaction of electrons with ion cores was represented by norm-conserving pseudopotential. The plane-wave cut off energy and Brillouin zone sampling were fixed at 770 eV and 5 \times 5 \times 2 Monkhorst-Pack-point meshes, respectively. The Broyden-Fletcher-Goldfarb-Shanno minimization method was used for geometry optimization, where the tolerances were selected as the difference in total energy within \( 1 \times 10^{-6} \text{ eV} \) per atom, maximum ionic Hellmann-Feynman force within \( 0.001 \text{ eV Å}^{-1} \), maximum ionic displacement within \( 5 \times 10^{-4} \text{ Å} \), and maximum stress within 0.02 GPa. The elastic constants were determined by the method reported by Milman et al. Vibrational frequencies were determined with the finite displacement method.

**Sample preparation.** Bulk Nb₄AlC₁₋ₓ (\( x \approx 0.3 \)) sample was synthesized by the method reported in Ref. 21. Briefly, Nb (~300 mesh), Al (~300 mesh) and graphite (D₉₀ = 6.5 μm) powders with a molar ratio of 4 : 1.2 : 2.7 were homogenized with agate balls and absolute alcohol in an agate jar for 12 h, and then dried at 70°C for 24 h. After that, the blended powders were cold compressed in a graphite mold. Finally, the green compact together with the mold were put into a hot pressing furnace and sintered at 1900°C for 1 h under a uniaxial pressure of 30 MPa with flowing Ar as protective gas.

**Composition and microstructure characterization.** Composition of thirty points in different regions of the as-prepared sample was analyzed by an electron-probe microanalyser (Shimadzu EPMA-1610, Kyoto, Japan). The phase components were investigated by XRD in an X-ray diffractometer (Rigaku D/max-2400, Tokyo, Japan) with Cu Kα radiation. The microstructural characterizations were performed on a transmission electron microscope (FEI Tecnai G² F20, Oregon, USA) working at 200 kV with an energy dispersive spectroscopy detector and a high-angle annular dark-field detector in the scanning transmission electron microscopy system. Selected area electron diffraction and CBED patterns were taken in Tecnai T12 (FEI Tecnai T12, Oregon, USA).

**Micro-Raman spectroscopic characterization.** Unpolarized and partially polarized Raman spectrums were collected at room temperature on a LabRAM HR800 (Horiba Jobin Yvon, France) equipped with an air-cooled CCD array detector in a backscattering geometry, and with diffraction gratings of 600 and 1800 lines per mm. A He–Ne laser (632.82 nm) with an incident power of 20 mW was used as excitation source. Theoretical Raman shifts were obtained by lattice dynamics calculation. According to Zhang et al., the peaks with \( A_{1g} \) symmetry disappear when \( \theta = 0° \) (\( \theta \) is the angle between the \( z \) axis of hexagonal crystal and that of the system coordinates). Therefore, the grains with \( \theta \approx 0° \) were chosen to collect the polarized and unpolarized Raman spectrums.

**Quasi-quenching.** Quasi-quenching was realized by a thermomechanical simulator, Gleeble 3800. The cooling rate above 800°C is near 200°C s⁻¹, as shown in Supplementary Fig. 3.

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Author Contributions

H.Z. carried out the sample synthesis, microstructure characterization and structure determination. T.H. conducted the first-principles calculations. Z.J.L. and M.M.H. collected the Raman spectrums. X.H.W. conceived and designed the project. H.Z., X.H.W., E.D.W. and Y.C.Z. wrote the paper. All authors contributed to data analysis and scientific discussion.

Additional Information

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