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Theoretical prediction, synthesis, and crystal structure determination of new MAX phase compound $V_2SnC$

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Abstract: Guided by the theoretical prediction, a new MAX phase $V_2SnC$ was synthesized experimentally for the first time by reaction of V, Sn, and C mixtures at 1000 °C. The chemical composition and crystal structure of this new compound were identified by the cross-check combination of first-principles calculations, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), and high resolution scanning transmission electron microscopy (HR-STEM). The stacking sequence of $V_2C$ and Sn layers results in a crystal structure of space group $P6_3/mmc$. The $a$- and $c$-lattice parameters, which were determined by the Rietveld analysis of powder XRD pattern, are 0.2981(0) nm and 1.3470(6) nm, respectively. The atomic positions are $V$ at $4f$ (1/3, 2/3, 0.0776(5)), Sn at $2d$ (2/3, 1/3, 1/4), and C at $2a$ (0, 0, 0). A new set of XRD data of $V_2SnC$ was also obtained. Theoretical calculations suggest that this new compound is stable with negative formation energy and formation enthalpy, satisfied Born–Huang criteria of mechanical stability, and positive phonon branches over the Brillouin zone. It also has low shear deformation resistance $c_{44}$ (second-order elastic constant, $c_{ij}$) and shear modulus ($G$), positive Cauchy pressure, and low Pugh’s ratio ($G/B = 0.500 < 0.571$), which is regarded as a quasi-ductile MAX phase. The mechanism underpinning the quasi-ductility is associated with the presence of a metallic bond.

Keywords: $V_2SnC$; new MAX phase compound; crystal structure; first-principles calculations

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1 Introduction

The layered machinable MAX phases are a large family of ternary carbides and nitrides with a general formula of $M_{n+1}AX_n$, where $M$ is an early transition metal, $A$ is a group of IIIA or IVA elements, $X$ is carbon or nitrogen, and $n$ is an integer, commonly equal to 1, 2, or 3 [1–3]. Structurally, the MAX phases can be regarded as alternatively stacking of transition metal carbide/nitride octahedra layers ($M_{n+1}X_n$) and $A$ group element layers [4–7]. Depending on the value of $n$, the $M_2AX$, $M_3AX_2$, and $M_4AX_3$ phases are referred to be 211, 312, and 413 phases, respectively. As is known to all, the majority of the 211 phases (e.g., $Cr_2AlC$, originally called “$H$-phases”) and two 312 phases (i.e., $Ti_3SiC_2$ and $Ti_3GeC_2$) were firstly reported by Nowotny et al. [8–10]. In 1999, the first 413 molecular composition, $Ti_4AlN_3$, was identified by Barsoum’s group [11]. Since then the MAX phase family has grown quite rapidly [1–7]. Subsequently, the $n$-value is not limited to 3, other etching out the group IIIA or IVA elements [12]. There are few studies about in V–Sn–C system. Most recently, only a series of A layers multi-element magnetic solid solution phases have received the most attention for two aspects: first, a recent study reports that $Ti_2SnC$ shows efficient recovery mechanical damage by crack self-healing characteristics after the oxidation at low temperature and short period [36]. Second, $Sn$-based MAX phases, particularly in the 211-stoichiometry ($M_2SnC$, $M = Ti, Zr, Hf$) might be potentially considered as electrical composites in reinforcement for metals and polymers.

In terms of the $A$ element, $Sn$-containing MAX phases have received the most attention for two aspects: first, a recent study reports that $Ti_2SnC$ shows efficient recovery mechanical damage by crack self-healing characteristics after the oxidation at low temperature and short period [36]. Second, $Sn$-based MAX phases, particularly in the 211-stoichiometry ($M_2SnC$, $M = Ti, Zr, Hf$) might be potentially considered as electrical composites in reinforcement for metals and polymers.

The stability of $V_2SnC$ was investigated and reported that this compound was intrinsically stable. Up to now, there is no experimental evidence for the existence of $V_2SnC$. Its crystal structure and a full set of XRD data remain unknown. Owing to the chemical similarity of constituent elements of MAX phases and considering the excellent electrical conductivity of other $Sn$-based MAX phases, such as $Ti_2SnC (14 × 10^6 \Omega^{-1} \cdot m^{-1})$ [35], the MAX phase $V_2SnC$ might be potentially considered as electrical composites in reinforcement for metals and polymers.

Considering these reported layered materials, new MAX phases and MAX phase-like compounds are still being synthesized and characterized [21–24]. Very recently, Sokol et al. [25] provided a comprehensive list of known MAX phases, bringing the total count to be 155. We note that some of important additions are the new ternary MAX phases: $Mn_2GaC$ [26], $Zr_2AlC$ [27], $NbGeC$ [28], $Hf_4AlC_2$ [29], and $V_4AlC_3$ [30].

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ceramics had graphite-like machinability. In order to raise the experiment to a theoretical level, Kanoun et al. [37] reported the theoretical study of properties of M2SnC (M = Ti, Zr, Hf, Nb) by first-principles calculations. Considering the properties of MAX phases, elastic properties are of particular importance as they determine the macroscopic characteristics of the material, such as friction and machinability [1–7]. However, the experimental characterization of elastic properties is hindered by the production of pure samples. This makes theoretical research a necessary tool for understanding the material properties.

The purpose of this study is to explore the existence of V2SnC and its crystal structure determination. Using a combination of first-principles calculations, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), and high resolution scanning transmission electron microscopy (HR-STEM), the lattice parameters and atomic positions were determined. We also report on the full XRD pattern data of V2SnC for the first time. Furthermore, the stability and elastic properties of V2SnC will also be presented and the mechanism for the quasi-ductility will be discussed based on electronic structure and chemical bonding analysis.

2 Theoretical and experimental details

2.1 Theoretical calculation

Before experimental verification, the possible existence of V2SnC was judged from the formation energy, formation enthalpy, elastic constants, and phonon dispersion curve. All the first-principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) code [38]. The exchange-correlation energy was treated under generalized gradient approximation (GGA) [39]. The plane-wave basis cutoff was 400 eV after convergent test and the special k-point sampling integration over the Brillouin zone was employed using the Monkhorst Pack method with 9 × 9 × 2 spatial k-point mesh [40]. Geometry optimization was achieved under the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme [41]. Lattice parameters and the atom positions are optimized until the total energy and maximum ionic displacement converged to 5 × 10–6 eV/atom and 5 × 10–4 Å, respectively. The calculations of the projected density of states were performed using a projection of the plane-wave electronic states onto a localized linear combination of atomic orbitals (LCAO) basis set.

The second-order elastic constants (cij) were determined from a linear fit of the calculated stress as a function of strain [42]. Four positive and four negative strains were applied for each strain component, with a maximum strain value of 0.3%. The criteria for convergence in optimizing atomic internal freedoms are: the difference on total energy within 5 × 10–6 eV/atom, the ionic Hellmann–Feynman forces within 0.002 eV/Å, and the maximum ionic displacement within 5 × 10–4 Å. The polycrystalline bulk modulus (B) and shear modulus (G) were calculated from the cij according to the Voigt, Reuss, and Hill approximations [43–45]. The phonon calculations were conducted with a finite displacement method.

2.2 Material synthesis

The starting materials for the synthesis of V2SnC are vanadium (99.9%, –300 mesh), tin (99.9%, –300 mesh), and graphite (99.9%, –300 mesh) powders. The powders were dryly-mixed in a V:Sn:C molar ratio of 2.0:1.1:1.0 in a resin jar for 24 h and sieved. Then the mixed powders were uniaxially pressed into a green compact using a steel die before putting into a graphite crucible. Reaction synthesis of V2SnC was conducted in a tube furnace under flowing Ar atmosphere at 1000 °C for 2 h (MXG1400-60, Micro-X Corp., China). After naturally cooling down to ambient temperature, the as-prepared powders were immersed in a diluted hydrochloric acid solution (2 mol·L–1, 200 mL) at room temperature for 10 h. Finally, the powders were washed in deionized water and dried in an oven.

Bulk V2SnC was prepared by spark plasma sintering (SPS) of the powder compact at 1000 °C for 30 min under an applied pressure of 40 MPa in the Ar atmosphere (SPS-20T-10, Chenhua Corp., China). Thereafter, the surface contaminations of the dense sample were removed by using a grinding wheel.

2.3 Crystal structure determination

Phase composition in V2SnC powders and bulk were identified by using an X-ray diffractometer (Bruker D8 A25X, Karlsruhe, Germany) with incident Cu Kα radiation (λ = 1.54178 Å). The step size was 0.02° and the scanning rate was 2 (°)/min. The microstructure of V2SnC was observed in a scanning electron microscope (FEI Inspect F50, USA) equipped with an energy dispersive spectrometer (Super Octane, USA). The stacking sequence of V2C and Sn layers was directly
observed in a high resolution scanning transmission electron microscope (HR-STEM, FEI Titan3 60-300, FEI Co., the Netherlands) equipped with a high-angle annular dark-field (HAADF) detector. Rietveld refinement was performed by utilizing the FULLPROF software package [46]. Theoretical XRD pattern of V2SnC was simulated using the Reflex powder diffraction code in the Accelrys Materials Studio program (Accelrys Inc., San Diego, USA). A full set of XRD patterns including reflection planes, peak positions, and intensities were obtained.

3 Results

3.1 Theoretical calculation of V2SnC

Figure 1 shows the crystal structure of V2SnC, which is built by replacing Nb in Nb2SnC [37] with V. After geometry optimization, the lattice constants and atom positions of the optimized structure are obtained, as listed in Table 1, which can be used as a reference for experimental investigations. For the possible existence evaluation, it can be justified from the formation energy, formation enthalpy, mechanical stability, and phonon dispersions over the Brillouin zone. The formation energy \( E_{\text{form}}(\text{V}_2\text{SnC}) \) can be determined from the total energy relative to the most stable polymorphic modifications of elements composing the compound.

\[
2V + Sn + C \rightarrow V_2SnC
\]

(1)

\[
E_{\text{form}}(\text{V}_2\text{SnC}) = \frac{1}{2} E_{\text{tot}}(\text{V}_2\text{SnC}) - \left( 2 \times \frac{1}{2} E_{\text{tot}}(V) + \frac{1}{8} E_{\text{tot}}(\text{Sn}) + \frac{1}{4} E_{\text{tot}}(C) \right)
\]

(2)

where \( E_{\text{tot}} \) is the total energy of the optimized structure of V2SnC, V, Sn, and graphite. \( E_{\text{form}}(\text{V}_2\text{SnC}) = -1.4834 \) eV < 0, indicating that V2SnC is possibly stable under normal conditions.

The thermodynamic stability at ambient pressure concerning decomposition is quantified in terms of the formation enthalpy. Considering that the general reaction mechanism of MAX phases is the reaction between MX and A compounds by inserting A atoms into MX carbide/nitride crystal structure, the formation enthalpy of V2SnC could be closely calculated by the following equation:

\[
\Delta H_{\text{form}}(\text{V}_2\text{SnC}) = H(\text{V}_2\text{SnC}) - H(\text{Sn}) - H(\text{V}_2\text{C})
\]

(4)

where \( \Delta H_{\text{form}}(\text{V}_2\text{SnC}) \) is the formation enthalpy of V2SnC. \( H(\text{V}_2\text{SnC}), H(\text{Sn}) \), and \( H(\text{V}_2\text{C}) \) are the enthalpy of V2SnC, Sn, and V2C, respectively. The calculated \( \Delta H_{\text{form}}(\text{V}_2\text{SnC}) \) is \(-0.0159 \) eV. The negative formation enthalpy indicates the possible existence of V2SnC phase.

Additionally, the mechanical stability of V2SnC was justified from the Born–Huang criteria [47]. For a hexagonal crystal, the conditions are expressed as

\[
c_{44} > 0 \quad c_{11} > |c_{12}|
\]

\[
(c_{11} + 2c_{12})c_{33} > 2c_{13}^2
\]

(5)

Table 2 lists the \( c_{ij} \) of V2SnC together with those of Ti2SnC, Zr2SnC, Hf2SnC, Nb2SnC, Cr2AlC, and Ti3SiC2 [37,48,49]. It is seen that the stability conditions of V2SnC are similar to those of MAX phases, demonstrating its stability under elastic strain perturbations.

---

**Fig. 1** Crystal structure of V2SnC.

**Table 1** Crystal structure parameters of V2SnC

| Formula     | V2SnC       |
|-------------|-------------|
| Crystal system | Hexagonal   |
| Space group  | P6/mnm (No. 194) |
| Formula unit | Z = 2       |
| Lattice parameters | First-principles calculations |
| a           | 0.3134      |
| c           | 1.2943      |
| Lattice constants (nm) | Rietveld refinement |
| a           | 0.2981(0)   |
| c           | 1.3470(6)   |
| Atomic positions | V 4f (1/3, 2/3, 0.0751) |
| Sn 2d (2/3, 1/3, 0.25) |
| C 2a (0, 0, 0) |
| C 2a (0, 0, 0) |

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Table 2 Theoretically predicted \(c_{ij}\), bulk modulus \((B)\), shear modulus \((G)\), Young’s modulus \((E)\), Poisson’s ratio \((v)\), and Pugh’s ratio \((G/B)\) for \(V_2\text{SnC}\), \(Ti_2\text{SnC}\), \(Zr_2\text{SnC}\), \(Hf_2\text{SnC}\), \(Nb_2\text{SnC}\), \(Cr_2\text{AlC}\), and \(Ti_3\text{SiC}_2\)

| Compound      | \(c_{11}\) (GPa) | \(c_{33}\) (GPa) | \(c_{44}\) (GPa) | \(c_{12}\) (GPa) | \(c_{13}\) (GPa) | \(c_{66}\) (GPa) | \(B\) (GPa) | \(G\) (GPa) | \(E\) (GPa) | \(v\) | \(G/B\) |
|---------------|------------------|------------------|------------------|------------------|------------------|------------------|-------------|-------------|-------------|-----|--------|
| \(V_2\text{SnC}\) | 336              | 304              | 85               | 126              | 122              | 105              | 190         | 95          | 244         | 0.286| 0.500  |
| \(Ti_2\text{SnC}\) [37] | 337              | 329              | 169              | 86               | 102              | 126              | 176         | 138         | 328         | 0.188| 0.784  |
| \(Zr_2\text{SnC}\) [37] | 269              | 290              | 148              | 80               | 107              | 94               | 157         | 110         | 268         | 0.215| 0.700  |
| \(Hf_2\text{SnC}\) [37] | 330              | 292              | 167              | 54               | 126              | 138              | 173         | 132         | 316         | 0.195| 0.763  |
| \(Nb_2\text{SnC}\) [37] | 341              | 321              | 183              | 106              | 169              | 118              | 209         | 126         | 314         | 0.250| 0.603  |
| \(Cr_2\text{AlC}\) [48,49] | 385              | 360              | 154              | 94               | 118              | 132              | 188         | 140         | 346         | 0.210| 0.718  |
| \(Ti_3\text{SiC}_2\) [48,49] | 354              | 344              | 165              | 91               | 103              | 131              | 183         | 141         | 337         | 0.193| 0.770  |

Besides, the stability of \(V_2\text{SnC}\) can also be judged from lattice dynamic investigations. As can be seen in the phonon dispersion and phonon density of state curves in Fig. 2, all phonon branches are positive, indicating the dynamical stability of this compound against mechanical perturbations.

3.2 Synthesis of \(V_2\text{SnC}\)

In Section 3.1, \(V_2\text{SnC}\) is theoretically predicted as a possible stable compound. To experimentally verify the existence, \(V_2\text{SnC}\) was synthesized through the reaction of vanadium, tin, and graphite powders. Figure 3(a) shows the XRD pattern of as-prepared powders synthesized at 1000 °C for 2 h (the XRD pattern of bulk is the same). In Fig. 3(a), Sn, and \(VC_{0.75}\) can be identified. In comparison with the simulated XRD pattern of \(V_2\text{SnC}\) in Fig. 3(b), which was generated using the Reflex powder diffraction code in Accelrys Materials Studio program, the peaks positioned at 13.174°, 26.517°, 40.277°, etc., which do not belong to either Sn or \(VC_{0.75}\), coinciding with those of \(V_2\text{SnC}\) in the simulated XRD pattern. Some small peaks, at ~34.934°, ~36.554°, ~51.536°, etc., remained unidentified (these unknown peaks are labeled on the pattern). This result demonstrates the presence of the new MAX phase \(V_2\text{SnC}\). Since \(V_2\text{SnC}\) has not been synthesized in the experiment, the study of this new compound is intriguing.

It is well known that MAX phases crystallize in hexagonal structure and their grains are generally layered hexagons [1–7,50] in morphology. To confirm that \(V_2\text{SnC}\) has a similar microstructure, the microstructure of as-prepared powders and SPS sintered bulk was observed by SEM. As can be seen from Fig. 4(a) (high magnification on the right), \(V_2\text{SnC}\) exhibits the microstructure of typical thin hexagons. From the fracture surfaces of the bulk sample, lamellar microstructure features can clearly be observed, as shown in Figs. 4(b) and 4(c). To further

![Fig. 2](image_url) Calculated phonon dispersion relations of \(V_2\text{SnC}\).

![Fig. 3](image_url) Comparison between XRD patterns of (a) powders synthesized through the reaction between V, Sn, and C at 1000 °C for 2 h and (b) the simulated one of \(V_2\text{SnC}\).
identify the composition of this compound, the representative compositions from different grains and positions determined by EDS are listed in Table 3. Although EDS analysis is semi-quantitative and accurate determination of light elements like C is difficult, the nominal ratio of V:Sn:C can approximately be assumed to be 2:1:1. The above results further confirmed that the new MAX phase compound V$_2$SnC is experimentally existing.

3.3 Determination of stacking sequence in V$_2$SnC

Previous studies demonstrated that the most efficient method to determine the stacking sequence in MAX phases is through STEM observation using Z-contrast image [4–6,51,52], wherein the stacking sequence of M and A layers can directly be revealed. Figure 5(a) presents a Z-contrast STEM image after fast Fourier transform (FFT) filtering, wherein the arrangement of the atoms on (1100) plane is revealed. Two layers of V interleaved by one layer of Sn is obvious and the lattice constant in c-direction is 1.347 nm. Atom arrangement on (1120) plane is shown in Fig. 5(b). Stacking sequences consisting of two layers of V interleaved by one layer of Sn are revealed, i.e., the stacking sequence of V and Sn follows ABAAB similar to that of other M$_2$AC phases [51–53], i.e., every two layers of V atoms and one layer of Sn atoms are alternately stacked along the [0001] direction. The structure can also be regarded as a Sn layer inserted into the twin boundary of V$_2$C, as shown in the inset structure model in Fig. 5, similar to the other MAX phases [51–53]. The combination of XRD analysis, SEM, and STEM observation confirmed that the synthesized new phase is V$_2$SnC. The synthesis of the V$_2$SnC MAX phase is significant because it provides experimental evidence for the existence of this new compound, which opens the window to explore more M$_2$AX phases in other compositions. It also provides more opportunities for composition design and property control of MAX phases.

3.4 New set of XRD data of V$_2$SnC

XRD pattern is important for phase identification and structure analysis. Since the XRD pattern of V$_2$SnC is not available in the literature, it is useful to obtain a new set of patterns for this compound. To achieve such a goal, the Rietveld refinement of powder XRD pattern

Table 3 Chemical compositions obtained from EDS analysis of V$_2$SnC grains

| Point number | V (at%) | Sn (at%) | C (at%) | Atomic ratio (V:Sn:C) |
|--------------|---------|----------|---------|----------------------|
| 1            | 48.01   | 22.99    | 29.00   | 2.09:1:1.44          |
| 2            | 46.00   | 22.14    | 31.86   | 2.08:1:1.44          |
| 3            | 45.86   | 23.02    | 31.11   | 1.99:1:1.35          |
| 4            | 46.58   | 22.58    | 30.84   | 2.06:1:1.35          |
of V<sub>2</sub>SnC was conducted at peak positions 2θ = 10°–80°. As shown in Fig. 6, the black crosses represent the experimental diffraction profile, while the red solid line denotes the theoretical pattern. The theoretical Bragg diffraction positions of V<sub>2</sub>SnC, Sn, and VC<sub>0.75</sub> are marked vertical purple, green, and orange lines, respectively. The blue curve is the deviation between the calculated and experimental XRD patterns. The obtained reliability factors are \( R_p = 8.27\% \) and \( R_wp = 12.34\% \), respectively, indicating good agreement between model and measured data. Detailed crystal structure information is depicted in Table 1. The space group of V<sub>2</sub>SnC is \( P6_3/mmc \) (No. 194) and the lattice constants are \( a = 0.2981(0) \) nm and \( c = 1.3470(6) \) nm. The atoms are located at: V 4f (1/3, 2/3, 0.0776(5)), Sn 2d (2/3, 1/3, 1/4), and C 2a (0, 0, 0). The difference between theoretical calculation and the Rietveld refinement is probably ascribed to the existence of defects in the crystal structure of V<sub>2</sub>SnC. Besides, a new set of XRD data including Bragg diffraction planes \((hkl)\), \(2\theta\), interplane distance \(d\), and intensities \(I\) of V<sub>2</sub>SnC are given in Table 4. These data are useful for phase identification and structural characterization of this new MAX phase V<sub>2</sub>SnC.

4 Discussion

In Section 3, a new MAX phase V<sub>2</sub>SnC was successfully synthesized for the first time. Its crystal structure was determined and a new set of XRD data was obtained. From the application point of view, it is intriguing to understand the specific properties of this compound, which allowed discussion on its elastic properties and mechanism that underpins these properties.

4.1 Quasi-ductility judged from elastic properties

In Table 2, the elastic properties of V<sub>2</sub>SnC are given, in which \( c_{11}, c_{33}, c_{44}, c_{12}, \) and \( c_{13} \) are independent, while \( c_{66} \) is not independent and is related to \( c_{11} \) and \( c_{12} \) through the following relationship:

\[
c_{66} = 1 / 2(c_{11} - c_{12})
\]

Comparing the second-order elastic properties of
Table 4 Calculated and experimental data of reflections, 2θ, d-spacings, and intensities of V2SnC.
The peaks of (006), (201), (202), and (204) were not observed due to their low intensities

| hkl | 2θ_exp (°) | 2θ_cal (°) | d_cal (Å) | d_obs (Å) | I_cal (%) | I_obs (%) |
|-----|------------|------------|-----------|-----------|-----------|-----------|
| 0 0 2 | 13.134 | 13.174 | 6.735 | 6.715 | 15.5 | 22.0 |
| 0 0 4 | 26.445 | 26.517 | 3.368 | 3.359 | 12.4 | 21.2 |
| 1 0 0 | 34.711 | 34.916 | 2.582 | 2.568 | 20.9 | 13.5 |
| 1 0 1 | 35.363 | 35.368 | 2.536 | 2.536 | 15.6 | 6.5 |
| 1 0 2 | 37.262 | 37.274 | 2.411 | 2.410 | 6.1 | 0.6 |
| 0 0 6 | 40.132 | — | 2.245 | — | 20.1 | — |
| 1 0 3 | 40.255 | 40.277 | 2.239 | 2.237 | 100.0 | 100.0 |
| 1 0 4 | 44.160 | 44.199 | 2.049 | 2.047 | 2.2 | 3.4 |
| 1 0 5 | 48.811 | 48.835 | 1.864 | 1.863 | 3.8 | 1.0 |
| 1 0 6 | 54.084 | 54.245 | 1.694 | 1.690 | 15.4 | 1.7 |
| 0 0 8 | 54.447 | 54.490 | 1.684 | 1.683 | 0.6 | 3.6 |
| 1 0 7 | 59.895 | 59.907 | 1.543 | 1.543 | 5.6 | 1.4 |
| 1 1 0 | 62.218 | 62.313 | 1.491 | 1.489 | 18.5 | 13.3 |
| 1 1 2 | 63.899 | 63.808 | 1.482 | 1.458 | 2.4 | 2.6 |
| 1 0 8 | 66.204 | 66.531 | 1.410 | 1.404 | 0.2 | 1.0 |
| 1 1 4 | 68.810 | 69.232 | 1.363 | 1.356 | 4.7 | 0.8 |
| 0 0 10 | 69.756 | 69.946 | 1.347 | 1.344 | 0.8 | 0.8 |
| 1 0 9 | 73.003 | 73.077 | 1.295 | 1.294 | 14.9 | 7.8 |
| 2 0 0 | 73.254 | 73.256 | 1.291 | 1.291 | 2.2 | 3.5 |
| 2 0 1 | 73.645 | — | 1.285 | — | 2.0 | — |
| 2 0 2 | 74.813 | — | 1.268 | — | 0.7 | — |
| 1 1 6 | 76.664 | 76.744 | 1.242 | 1.241 | 16.3 | 11.1 |
| 2 0 3 | 76.746 | 77.001 | 1.241 | 1.237 | 13.4 | 6.3 |
| 2 0 4 | 79.427 | — | 1.206 | — | 0.5 | — |

V2SnC to those of Ti2SnC, Zr2SnC, Hf2SnC, and Nb2SnC, it is found that they have similar elastic constants c11, c33, c12, and c13. However, the shear deformation resistance c44 of V2SnC (85 GPa) is much lower than those of Ti2SnC (169 GPa), Zr2SnC (148 GPa), Hf2SnC (167 GPa), and Nb2SnC (183 GPa) [37]. The c44 of V2SnC is also lower than the well-investigated MAX phases of Cr2AlC (154 GPa) and Ti3SiC2 (165 GPa) [48,49]. Low c44 indicates easy shear deformation along [110] (0001). Low shear deformation of V2SnC is also reflected from G, which represents the resistance to shape change of the polycrystalline material. The G of V2SnC is 90 GPa, which is much lower than those of Ti2SnC (138 GPa), Zr2SnC (110 GPa), Hf2SnC (132 GPa), Nb2SnC (126 GPa), Cr2AlC (140 GPa), and Ti3SiC2 (141 GPa) [37,48,49]. Low shear deformation is a characteristic of damage tolerant or quasi-ductile ceramics, which can also be judged from the Cauchy pressure and Pugh’s shear to G/B [54]. For a hexagonal material, the Cauchy pressure is defined as: \( P_c = c_{13} - c_{44} \) and \( P_a = c_{11} - c_{12} \). In general, a positive Cauchy pressure is an indication of ductile behavior. For this new MAX phase V2SnC, Cauchy pressure is positive and in both a- \( (P_a = +37 \text{ GPa}) \) and c- \( (P_c = +21 \text{ GPa}) \) directions, indicating that V2SnC is ductile in both a- and c-directions. Considering that the experimentally proved MAX phases like Ti2SnC \( (P_a = -67 \text{ GPa}, P_c = -40 \text{ GPa}) \), Zr2SnC \( (P_a = -41 \text{ GPa}, P_c = -14 \text{ GPa}) \), Hf2SnC \( (P_a = -41 \text{ GPa}, P_c = -84 \text{ GPa}) \), Nb2SnC \( (P_a = -14 \text{ GPa}, P_c = -12 \text{ GPa}) \), Cr2AlC \( (P_a = -36 \text{ GPa}, P_c = -38 \text{ GPa}) \), and Ti3SiC2 \( (P_a = -62 \text{ GPa}, P_c = -40 \text{ GPa}) \) have negative Cauchy pressure, positive Cauchy pressure is the characteristic that distinguishes this new MAX phase V2SnC from other MAX phases. Ductile behavior can also be judged from Pugh’s shear to G/B. Low G/B (< 0.571) indicates intrinsic ductility. The G/B of V2SnC is 0.500, which is lower than the criterion 0.571 and those of most MAX phases and MAX phase-like materials [2–7,50,55], revealing that V2SnC is an intrinsic ductile MAX phase. Because there are no five independent slip systems for MAX phases, we still call this new MAX as quasi-ductile material.

4.2 Mechanism of quasi-ductility

It has come to light that the elastic properties of MAX phases are underpinned by their electronic structure and chemical bonding. To gain more insight into the mechanism of the ductile behavior of this new MAX phase, the electronic structure of V2SnC is investigated. Figure 7 shows the band structure of V2SnC and the projected density of states of V, Sn, and C atoms. Similar to other MAX phases and MAX phase-like compounds [2–7,49,55], overlapping between valence and conduction bands across the Fermi level is clearly seen in H–K, K–Γ, and Γ–M directions in Fig. 7(a), revealing that V2SnC is electrically conductive in both a–b plane and c-direction. However, the overlapping is anisotropic with less overlapping in H–K direction, indicating that the electrical conductivity is anisotropic. Overlapping between valence and conduction bands across the Fermi level also reveals the presence of metallic bonding, which is the origin of the quasi-ductility of V2SnC. The difference of Cauchy pressure in a- and c-direction \( (P_a = +37 \text{ GPa} \) and \( P_c = +21 \text{ GPa} \)) can be attributed to the anisotropic metallic bonding.
As can be seen from Fig. 7(b), the main contribution to the electrical conductivity comes from V 3d states and Sn 5p states. In Figs. 7(c) and 7(d), it is seen that V 3d $t_{2g}$ and V 3d $e_g$ electrons mainly contribute to the electrical conductivity and there is minor contribution from Sn 5p$_z$ electrons.

Easy shear deformation along [11\bar{2}0]//(0001) can also be understood from the electronic structure and chemical bonding in V$_2$SnC. In Fig. 8(a), strong covalent-ionic V–C bond is formed through overlapping between V 3d $t_{2g}$ and C 2p$_x$ orbitals in the low energy range from –6 to –3 eV. In Fig. 8(b),

![Fig. 7](image_url)  
(a) Band structure of V$_2$SnC; (b) projected density of V, Sn, and C atom states; (c, d) electron density maps on (11\bar{2}0) plane of V$_2$SnC near Fermi level. V 3d $e_g$ like, V 3d $t_{2g}$ like, and Sn 5p$_z$ like orbitals can be seen in Figs. 7(c) and 7(d), respectively. A 2 × 2 × 1 cell is used and the unit is electron/Å$^3$.

![Fig. 8](image_url)  
Electron density maps on (11\bar{2}0) plane of V$_2$SnC from (a) –6 to –3 eV and (b) –3 to –1 eV below the Fermi level, and the unit is electron/Å$^3$. 

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however, the interaction between V 3d eg and Sn 5p z orbitals is very weak and is metallic like in higher energy range from –3 to –1 eV. The weak V–Sn bonding can also be seen from the projected density of state curve in Fig. 7(b), wherein the V 3d and Sn 5p states are not overlapping although they are very close, demonstrating the weak interaction between them and the possible excellent quasi-plastic behavior.

5 Conclusions

In conclusion, the above results provide the existing evidence of MAX phase V2SnC using theoretical prediction and experimental verification. Theoretically, the possible existence of this compound was predicted from the negative formation energy and formation enthalpy, satisfied Born–Huang criteria of mechanical stability, and positive dispersions of all phonon branches over the Brillouin zone. Experimentally, this new MAX phase was synthesized for the first time by heating the V, Sn, and C starting powder mixture at 1000 °C. V2SnC exhibits a typical laminar microstructure similar to other MAX phases. The V2C and Sn layers are alternatively stacked along the [0001] direction. The lattice parameters are a = 0.2981(0) nm and c = 1.3470(6) nm, and the atomic positions are V 4f (1/3, 2/3, 0.0776(5)), Sn 2d (1/3, 2/3, 1/3, 1/4), and C 2a (0, 0, 0). Also, a new set of XRD data of V2SnC was obtained, which is useful for further phase identification and structure analysis. First-principles calculations indicated that this new MAX phase of V2SnC has low shear deformation resistance c44 and G, positive Cauchy pressure, and low G/B = 0.500 < 0.571, which could be judged as a quasi-ductile ceramic. The mechanism underpinning the quasi-ductility is the presence of metallic bond, dominated by the V 3d electrons near the Fermi level as well as the contribution of Sn 5p electrons.

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