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Research Article

X-site nitrogen engineering of V₂GaC MAX phase for enhanced microwave absorption

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ABSTRACT: The increasing proliferation of 5G/6G communication systems and artificial intelligence technologies has intensified electromagnetic pollution, creating an urgent demand for lightweight, efficient, and thermally stable electromagnetic wave (EMW) absorbers. MAX phases have emerged as promising candidates owing to their unique layered structures and excellent electrical conductivity; however, performance optimization has largely focused on M- and A-site engineering, while X-site regulation remains largely unexplored. Herein, a series of X-site nitrogen-substituted MAX phases, $V_2GaC_{1-x}N_x$ ($x = 0.25, 0.5, 0.75$, and 1), were successfully synthesized and their EMW absorption behaviors systematically investigated. Benefiting from nitrogen-induced modulation of the electronic structure and dielectric response, $V_2GaC_{0.75}N_{0.25}$ achieved an exceptional minimum reflection loss (RL_{min}) of -71.87 dB at an ultrathin thickness of 1.26 mm, while $V_2GaC_{0.25}N_{0.75}$ exhibited a maximum effective absorption bandwidth (EAB) of 5.2 GHz. Furthermore, efficient EMW attenuation covering the entire $2-18$ GHz frequency range was achieved through thickness modulation. Notably, pro-oxidized V_2GaN still maintains excellent microwave absorption performance when measured at room temperature after oxidation treatment at 500 °C, exhibiting an RL_{min} of -60.89 dB and an EAB of 3.59 GHz, demonstrating excellent thermal stability of its electromagnetic response. This work demonstrates that X-site nitrogen engineering can effectively regulate the electromagnetic response of V_2GaC MAX phase, providing an compositional strategy for the design of high-performance V_2GaC microwave

absorbers while offering valuable theoretical insights for X-site engineering in other MAX-phase systems.

KEYWORDS: electromagnetic wave absorption, $V_2\text{GaC}_{1-x}\text{N}_x$ solid solution, X-site engineering, dielectric polarization, impedance matching

1. Introduction

The rapid development of 5G/6G communications, the Internet of Things, artificial intelligence, high-power microwave technologies, and advanced electronic information systems has intensified electromagnetic pollution, creating increasing demands for efficient electromagnetic wave (EMW) absorbers [1, 2]. Beyond strong attenuation, practical absorbers must simultaneously achieve efficient impedance matching, broadband response, low thickness and weight, and long-term stability under harsh environments [3-5]. In this context, the key scientific challenge is to establish effective strategies for simultaneously regulating electromagnetic-wave entry and energy dissipation through rational control of material composition and structure.

EMW absorbers dissipate incident electromagnetic energy through dielectric loss and/or magnetic loss, including conductive loss, dipolar and interfacial polarization, and multiple scattering. Effective absorption therefore requires a delicate balance between impedance matching and attenuation capability [6-8]. Among emerging absorber systems, MAX phases, with the general formula $M_{n+1}AX_n$ (where M is an early transition metal or lanthanide elements, A is a main group or subgroup element, X is C, N, and/or B, and $n = 1-4$), have attracted considerable attention owing to their distinctive combination of metallic and ceramic characteristics [9, 10]. Their high electrical conductivity, thermal and chemical stability, oxidation resistance, mechanical strength, and intrinsically layered crystal structures make them particularly attractive for electromagnetic applications [11-14]. More importantly, the electronically anisotropic MX-A layered framework and substantial compositional flexibility provide opportunities for manipulating charge transport, polarization processes, electromagnetic parameters, and impedance matching

For MAX phases, whose microwave absorption is predominantly governed by dielectric-loss, the electromagnetic response is closely associated with the electronic structure and charge-transport characteristics of the MX framework. Consequently, compositional engineering has emerged as an effective approach for optimizing their electromagnetic properties [15-17]. To date, however, such efforts have been overwhelmingly centered on M- and A-site engineering. A variety of M-site modifications, including Sc_2GaC [18], $(\text{Cr}_{0.5}\text{V}_{0.5})_4\text{AlC}_3$ [19], $(\text{V}_{1-x}\text{Ti}_x\text{Cr}_y)_2\text{AlC}$ [20], and $(\text{Ti}_{1/4}\text{V}_{1/4}\text{Zr}_{1/4}\text{Nb}_{1/4})_2\text{AlC}$ [21], have demonstrated improved reflection loss and absorption bandwidth relative to their parent MAX phases. Likewise, A-site engineering has demonstrated remarkable effectiveness. For example, the high-entropy MAX phase $\text{Ti}_2(\text{Al}_{1/5}\text{Sn}_{1/5}\text{In}_{1/5}\text{Bi}_{1/5}\text{Ag}_{1/5})\text{C}$ achieved an $\text{RL}_{\min}$ of -71.6 dB at a thickness of only 1.25 mm while maintaining excellent oxidation resistance [22]. These studies establish M- and A-site engineering as powerful and relatively mature strategies for tailoring the electromagnetic response of MAX phases.

Despite these advances, current research has been overwhelmingly concentrated on M-site and A-site regulation, whereas X-site engineering remains largely unexplored. Considering that the X-site directly participates in the formation of the MX octahedral framework and strongly influences the electronic structure, chemical bonding, and charge-transport behavior of MAX phases, X-site modification is expected to provide a fundamentally different route for tuning electromagnetic properties. Notably, nitrogen-containing MAX phase reported in recent years have already exhibited exceptional microwave absorption performance, suggesting that nitrogen incorporation may represent a highly promising yet underexplored strategy for absorber design. Nevertheless, systematic investigations into the influence of X-site nitrogen substitution on the electromagnetic properties and underlying mechanisms of MAX phases remain scarce.

In contrast, X-site engineering remains relatively underexplored, primarily due to its intrinsic structural and synthetic constraints. Unlike the relatively weakly bonded A layers, X atoms constitute the core MX octahedral framework and are strongly coupled

with M atoms through robust M–X bonds. Consequently, X-site substitution or alloying directly perturbs the fundamental crystal framework of MAX phases and is subject to stringent constraints imposed by phase stability, local coordination, atomic-size mismatch, and chemical bonding. More importantly, compared with M- and A-site engineering, which can generally be achieved through relatively accessible compositional tuning or solid-solution strategies, X-site regulation requires precise control over the C/N chemical potential and the formation of stable M–X octahedral configurations, making homogeneous and continuous X-site modification substantially more challenging. These intrinsic structural and synthetic constraints have led X to be regarded as a relatively fixed component of MAX phases, leaving its potential for electromagnetic-property regulation largely unexplored. X-site chemistry directly participates in M–X bonding and can further modulate electronic states, charge transport, lattice distortion, defect formation, and polarization behavior. Therefore, X-site engineering offers a promising opportunity to move beyond the conventional M/A-site regulation paradigm, providing a new degree of freedom for the synergistic optimization of dielectric loss and impedance matching and, consequently, opening a new materials-design dimension for enhancing the microwave absorption performance of MAX phases.

Herein, we introduce an X-site nitrogen-engineering strategy to systematically regulate the electromagnetic properties of V₂GaC-based MAX phase. By constructing a series of V₂GaC_{1-x}N_x ($x=0.25, 0.5, 0.75$, and 1) solid solutions absorbers. Among the investigated compositions, V₂GaC_{0.75}N_{0.25} exhibited outstanding absorption performance, delivering a RL_{min} of -71.87 dB at an ultrathin matching thickness of 1.26 mm, whereas V₂GaC_{0.25}N_{0.75} achieves a broad EAB of 5.2 GHz. Furthermore, the entire V₂GaC_{1-x}N_x series maintains over 90% absorption efficiency ($RL < -10$ dB) across a wide frequency range of 4–18 GHz by tuning absorber thickness from 1 to 5 mm. In addition, V₂GaN demonstrates excellent stability against high-temperature, retaining strong microwave absorption performance at room temperature when oxidation treatment at 300 °C, 400 °C, and 500 °C, with RL_{min} values of -61.83 dB, -55.83 dB,

and -60.89 dB, respectively. The results reveal that X-site N incorporation reconstructs the local bonding environment and electronic structure of the MAX phase, thereby tailoring its electromagnetic response and enabling enhanced microwave absorption.

2. Experimental procedure

2.1 Synthesis of $V_2GaC_{1-x}N_x$ MAX Phases

High-purity starting materials were employed throughout this study. Vanadium (V) powder (≈ 325 mesh, 99.99% purity) and vanadium nitride (VN) powder (≈ 325 mesh, 99.9% purity) were purchased from Shanghai Aladdin Co., Ltd. Graphite (C) powder (≈ 325 mesh, 99.95% purity) was obtained from Macklin, Inc. and Tianjin Hengxing Reagent Co., Ltd., China. Gallium (Ga) was supplied in the form of metal pellets (99.5 wt%, approximately 3 mm in diameter) by the Target Research Center of the General Research Institute for Nonferrous Metals, Beijing, China.

For the synthesis of the V_2GaC MAX phase, elemental powders were weighed according to a molar ratio of V:Ga:C = 2:1.1:0.9 [23]. The V and C powders were first mixed and ground for 30 minutes, followed by the addition of Ga pellets. The resulting mixture was transferred to an alumina crucible and heated in a tube furnace under a protective atmosphere. The temperature was increased to 1200 °C at a rate of 5 K/min and maintained for 7 hours. For the synthesis of V_2GaN , VN was employed as both the V and N source, while additional V powder and Ga pellets were introduced to adjust the overall elemental stoichiometry. Accordingly, the nominal starting composition was set to V:Ga:VN = 2:1.1:1. The sintering temperature was systematically varied between 1100 °C and 1400 °C, while all other processing parameters remained unchanged.

A series of $V_2GaC_{1-x}N_x$ ($x = 0.25, 0.5$, and 0.75) solid-solution MAX phases were subsequently prepared. Here $x = 0$ and $x = 1$ correspond to V_2GaC and V_2GaN , respectively. These precursor mixtures were formulated with molar ratios of V:Ga:C:VN = 2:1.1:1:0 ($x = 0$), 1.25:1.1:1:0.25 ($x = 0.25$), 1.5:1.1:0.5:0.5 ($x = 0.5$), 1.75:1.1:0.25:0.75 ($x = 0.75$), and 1:1.1:0:1 ($x = 1$). The obtained compositions were denoted as V_2GaC (N0), $V_2GaC_{0.75}N_{0.25}$ (N25), $V_2GaC_{0.5}N_{0.5}$ (N50), $V_2GaC_{0.25}N_{0.75}$

(N75), and V_2GaN (N100), respectively. For each synthesis batch, five pelletized samples were placed in the same alumina crucible and heated in a tube furnace. The furnace temperature was raised to 1300 °C, held for 7 hours, and subsequently cooled to room temperature at a rate of 5 °C/min.

In addition, oxidation-pretreatment experiments were performed in a tube furnace to evaluate the high-temperature oxidation resistance of V_2GaN powder. A 0.5 g of V_2GaN powder was loaded into an open alumina crucible, heated to target temperatures of 300 °C, 400 °C and 500 °C at 10 K/min. Heating was terminated immediately once each target temperature was attained. The specimens were furnace-cooled to room temperature before being retrieved, yielding pre-oxidized V_2GaN specimens subjected to different thermal-oxidation treatments.

2.2 Characterization

The phase composition of the synthesized MAX phases was identified by X-ray diffraction (XRD). XRD patterns were collected using a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu K α radiation over a 2θ range of 5°-80°, employing a step size of 0.02° and a counting time of 1 s per step. Microstructural observations and elemental analyses were carried out using a field-emission scanning electron microscope (SEM) (QUANTA 250 FEG microscope, FEI, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. Transmission electron microscopy (TEM) investigations were performed using an FEI Tecnai G2 F20S-TWIN microscope equipped with an EDS system. High-resolution scanning transmission electron microscopy high-angle annular dark-field (HRSTEM-HAADF) imaging was conducted at an accelerating voltage of 300 kV. The chemical states and bonding environments of the elements were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS SUPERA+, Shimadzu, Japan) with an energy step size of 0.025 eV. Simultaneous thermogravimetric-differential scanning calorimetry (TGA-DSC, STA) measurements were performed on a NETZSCH STA 449 F3 Jupiter instrument (Germany). The raw experimental data were processed using the NETZSCH Proteus® software (Version 8.0). Approximately 10 mg V_2GaN powder was loaded into an

alumina crucible, heated from room temperature to 1300 °C at 10 °C/min under flowing air atmosphere, with no isothermal holding time upon arriving at the maximum temperature. TGA mass-change and DSC heat-flow signals were recorded synchronously.

2.3 Absorption Performance Testing

The complex permittivity and permeability were measured using a vector network analyzer (Ceyear 3672B, Nanjing Dacheng Electronics Co., Ltd.). For each measurement, the MAX phase powder was mixed with paraffin wax at a mass ratio of 7:3. To ensure homogeneous dispersion, the mixture was first ground and dispersed in hexane. After evaporation of the solvent, the composite powder was cold-pressed into toroidal specimens with an outer diameter of 7 mm, an inner diameter of 3.04 mm, and a thickness of approximately 2 mm under a pressure of 5 MPa. This procedure ensured uniform distribution of the $V_2GaC_{1-x}N_x$ ($x = 0, 0.25, 0.5, 0.75, 1$) particles throughout the paraffin matrix. The reflection loss (RL) values were calculated based on transmission line theory according to the following formula [24]:

$$RL(dB)=20\log\left|\frac{Z_{in}-Z_0}{Z_{in}+Z_0}\right| \quad (1)$$

$$Z_{in}=Z_0\sqrt{\frac{\mu_r}{\epsilon_r}}\tanh\left[j\left(\frac{2\pi}{c}\right)fd\sqrt{\mu_r\epsilon_r}\right] \quad (2)$$

where Z_{in} , is the input impedance of the absorber, Z_0 is the impedance of free space, c is the speed of light in vacuum, f is the frequency of the incident electromagnetic wave, and d is the absorber thickness. ϵ and μ denote the complex relative permittivity and permeability, respectively.

2.4 Density Functional Theory Calculations

First-principles calculations were performed using the CASTEP package within the framework of density functional theory (DFT) [25]. Phonon spectra were calculated using the finite-displacement method. The exchange-correlation interactions were described using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [26]. Ultrasoft pseudopotentials were employed to represent the electron–ion interactions, and Brillouin-zone sampling was carried out using a Monkhorst–Pack k-point mesh of $10 \times 10 \times 2$. The self-consistent field (SCF)

convergence criterion was set to 5.0×10^{-7} eV/atom. Geometry optimization was considered converged when the total energy change, maximum atomic force, maximum stress, and maximum atomic displacement were less than 5.0×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively.

To investigate the effect of C/N substitution, $2 \times 2 \times 1$ supercell model of the $V_2GaC_{1-x}N_x$ were constructed for $x=0, 0.25, 0.5, 0.75$, and 1, as illustrated in Figure 1a. The formation energy was calculated according to:

$$\Delta E_{\text{form}} = E_{\text{total}}(V_2GaC_{1-x}N_x) - 2E_{\text{atom}}(V) - E_{\text{atom}}(Ga) - (1-x)E_{\text{atom}}(C) - xE_{\text{atom}}(N)$$

Where $E_{\text{total}}(V_2GaC_{1-x}N_x)$ represents the total energy of the primitive cell, corresponding to one-quarter of the total energy of the $2 \times 2 \times 1$ supercell. E_{atom} denotes the energy per atom of the elemental reference state (in eV/atom). The reference states were chosen as the most stable phases under standard conditions, namely body-centered cubic (bcc) V, α -Ga, diamond-structured C, and gaseous N_2 , with the atomic energy of N taken as one-half of the total energy of an N_2 molecule.

2.5 Computational Simulations

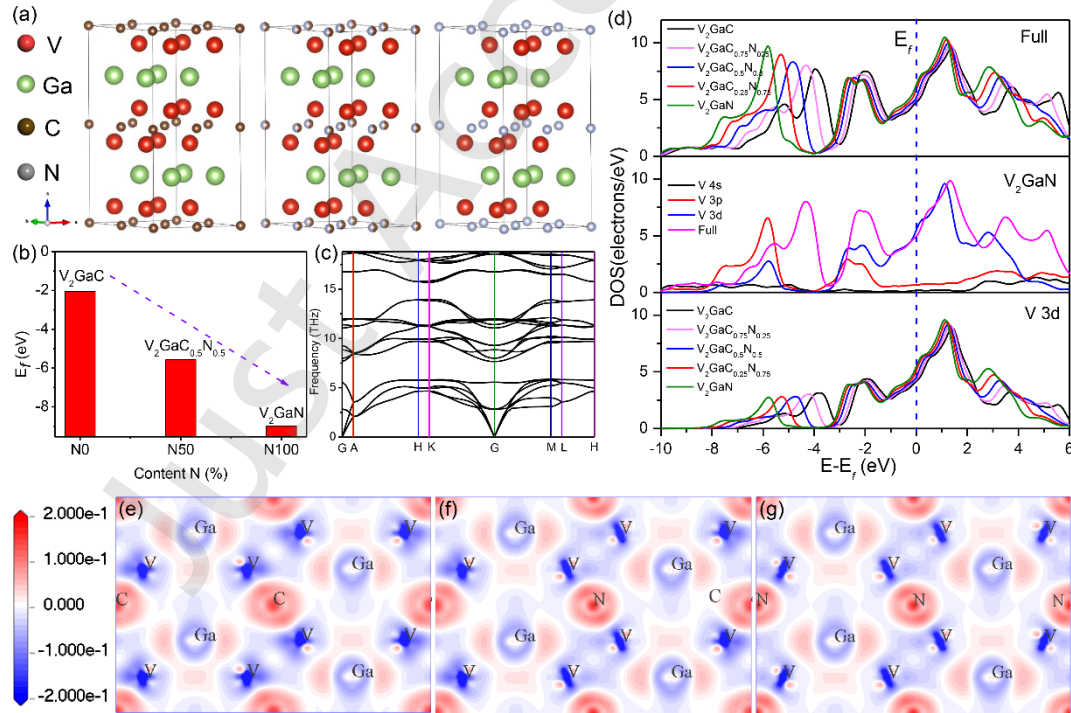
The radar cross section (RCS) simulations were performed at a frequency of 13.5 GHz. Based on the widely adopted metal-backed absorber model, a perfect electric conductor (PEC) substrate coated with the absorber layer was constructed on the Y-O-Z plane. The incident plane wave (PW) propagated along the negative X-direction, i.e., from the positive to the negative X-axis. The dimensions of the PEC substrate and absorber layer were set to $200 \times 200 \times 1$ and $200 \times 200 \times 1.5$ mm³, respectively. Boundary conditions were applied along the x, y, and z directions, with open (add space) boundaries imposed in all directions to eliminate artificial reflections from the computational domain. In the RCS simulations, θ and ϕ represented the elevation angle and azimuth angle of observation, respectively.

3. Results and discussion

3.1 Design of Nitrogen- substituted MAX Phase Absorbing Materials

The successful synthesis of V_2GaC [23] and V_2GaN [27] has been reported previously. To evaluate the structural stability prior to experimental synthesis, density

functional theory (DFT) calculations were performed on $V_2GaC_{1-x}N_x$ ($x=0, 0.5$, and 1). The optimized crystal structures of V_2GaC , $V_2GaC_{0.5}N_{0.5}$, and V_2GaN are shown in Fig. 1(a). As the N concentration increases, N atoms progressively occupy the X sites of the MAX phase lattice while maintaining the layered hexagonal framework, indicating that the crystal structure can accommodate substantial C/N substitution without significant lattice distortion. The calculated formation energies are summarized in Fig. 1(b). The formation energy decreases monotonically with increasing N content, changing from approximately -2.5 eV for V_2GaC (N0) to nearly -9 eV for V_2GaN (N100). The increasingly negative formation energy indicates enhanced thermodynamic stability upon N incorporation. This result suggests that the V–N bond is energetically more favorable than the V–C bond, which can be attributed to the stronger orbital hybridization and higher bond strength between V and N atoms. The dynamical stability of the $V_2GaC_{1-x}N_x$ structure was further evaluated through phonon dispersion



calculations. As shown in Fig. 1(c), no imaginary frequencies are observed throughout the entire Brillouin zone, confirming the dynamical stability of the investigated structure. The absence of soft phonon modes indicates that the crystal framework remains stable after C/N substitution, supporting the feasibility of synthesizing the corresponding solid-solution phases experimentally.

Fig. 1 (a) The crystal structures and electronic structure of $V_2GaC_{1-x}N_x$ MAX phases. (a) The crystal structures of the V_2GaC , $V_2GaC_{0.5}N_{0.5}$, and V_2GaN MAX phases are simulated from left to right. (b) The calculated formation energy (E_f) of V_2GaC , $V_2GaC_{0.5}N_{0.5}$, and V_2GaN MAX phase. (c) calculated phonon dispersion of V_2GaN . (d) Projected density of $V_2GaC_{1-x}N_x$ ($x=0, 0.25, 0.5, 0.75$, and 1). Calculated valence electron density of V_2GaC (e), $V_2GaC_{0.5}N_{0.5}$ (f) and V_2GaN (g) in the (110) plane. This plane was selected to visualize the V, Ga, and C/N bonding scheme.

Figure 1(d) presents the total and projected density of states (DOS) of $V_2GaC_{1-x}N_x$. For all compositions, finite electronic states are observed at the Fermi level ($E_n = 0$ eV), indicating intrinsic metallic behavior. The electronic states near the Fermi level are dominated by V 3d orbitals, whereas contributions from V 4s and V 3p states are relatively minor. Such electronic characteristics are typical of MAX phases and imply excellent electrical conductivity [28]. With increasing nitrogen content, the DOS distribution around the Fermi level gradually shifts and broadens. In particular, the hybridization peaks located between -6 and -2 eV become more pronounced, indicating strengthened interactions between V 3d states and X-site (C/N) p orbitals. The enhanced orbital overlap suggests increased electron delocalization and stronger chemical bonding, which is consistent with the trend observed in the formation energy calculations. Moreover, the preservation of a high DOS near the Fermi level implies that N substitution does not deteriorate the metallic conductivity of the system.

To further understand the bonding evolution, differential charge density distributions were calculated, as shown in Figs. 1(e)-1(g). Significant charge accumulation is observed around the X-site atoms and along the V–X bonding direction, while charge depletion mainly occurs around the V atoms, indicating electron transfer from V toward the non-metallic C/N atoms. Compared with V_2GaC , the charge accumulation surrounding N atoms becomes noticeably stronger in the N-containing structures, reflecting the higher electronegativity of N relative to C. Consequently, the V–N bonds exhibit a stronger covalent/ionic mixed-bonding character than the V–C bonds [29]. The enhanced charge localization around N atoms corroborates the increased thermodynamic stability and stronger orbital hybridization revealed by the formation energy and DOS analyses. Overall, the DFT results demonstrate that nitrogen substitution significantly strengthens the V–X bonding interaction, lowers the

formation energy, and preserves the metallic nature of the $V_2GaC_{1-x}N_x$ solid solutions. These characteristics are expected to facilitate charge transport and interfacial polarization, which may contribute positively to the electromagnetic-wave attenuation capability of the MAX phase material.

3.2 Fabrication of Nitrogen-substituted $V_2GaC_{1-x}N_x$ MAX Phases

The phase evolution and crystal structures of the synthesized products were systematically investigated by XRD, as shown in Fig. 2. Figure 2(a) presents the XRD patterns of V_2GaN samples synthesized at different temperatures. Distinct diffraction peaks corresponding to the V_2GaN MAX phase [27] are observed in all samples, accompanied by minor impurity phases, primarily VN and V_2N . As the synthesis temperature increases from 1100 to 1400 °C, the diffraction intensity of the V_2GaN phase initially increases and subsequently decreases, indicating a gradual increase in phase purity followed by partial decomposition at elevated temperatures. In contrast, the diffraction peaks associated with the secondary nitride phases exhibit an opposite trend. Among all samples, the specimen synthesized at 1300 °C displays the highest relative intensity of V_2GaN reflections and the lowest impurity content, suggesting that this temperature provides the optimal balance between reaction kinetics and phase stability. At lower temperatures, insufficient atomic diffusion and incomplete reactions hinder the formation of the MAX phase, whereas excessive temperatures promote the decomposition of V_2GaN and the generation of vanadium-rich nitride byproducts.

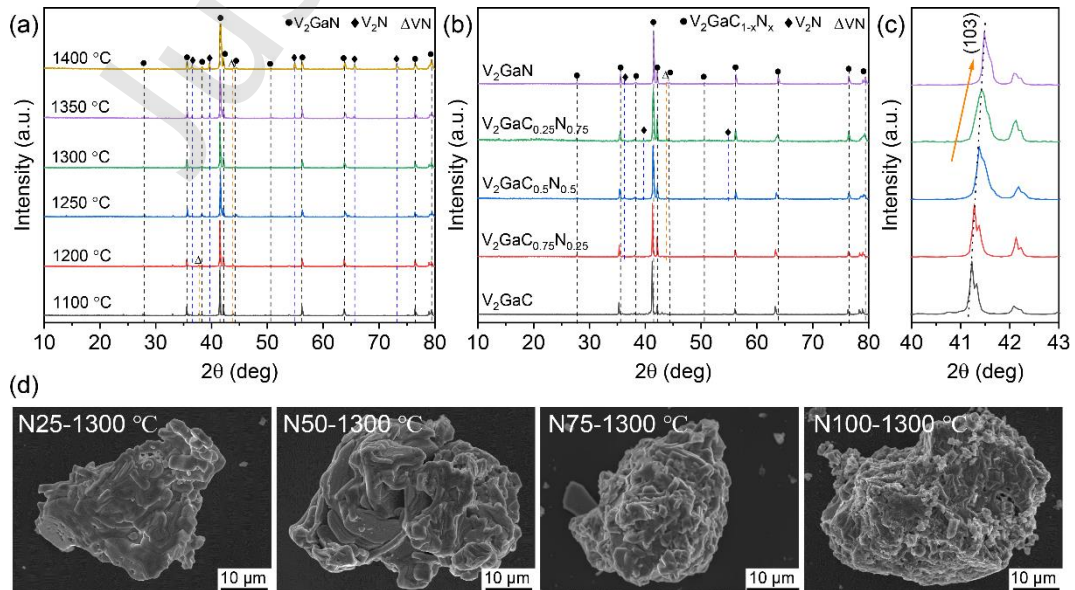


Fig. 2 Phase compositions and microstructure of $V_2GaC_{1-x}N_x$ MAX phases. (a) XRD patterns of V_2GaN with different temperatures. XRD patterns of $V_2GaC_{1-x}N_x$ ($x=0, 0.25, 0.5, 0.75$, and 1) (b) and (c) enlarged XRD patterns of (103) planes in (b). SEM images of N25, N50, N75, and N100, respectively.

The influence of nitrogen substitution on the crystal structure was further examined in the $V_2GaC_{1-x}N_x$ system. As shown in Fig. 2(b), all characteristic diffraction peaks gradually shift with increasing nitrogen content without the appearance of additional diffraction peaks, indicating the formation of a single-phase solid solution rather than a physical mixture of V_2GaC and V_2GaN . The continuous peak evolution across the entire composition range demonstrates that nitrogen atoms are successfully incorporated into the X-site lattice and progressively replace carbon atoms. Notably, the diffraction peaks systematically shift toward higher 2θ angles as the nitrogen content increases. According to Bragg's law, this behavior reflects a reduction in interplanar spacing caused by lattice contraction. Since nitrogen possesses a smaller atomic radius than carbon, substitution of C by N leads to a decrease in lattice parameters, particularly along the c -axis [30, 31]. Figure 2(c) further highlights the progressive shift of the (103) reflection toward higher diffraction angles with increasing N concentration, exhibiting a Vegard-like structural evolution and providing compelling evidence for the successful formation of $V_2GaC_{1-x}N_x$ solid-solution MAX phases. The microstructural characteristics of the samples synthesized at 1300 °C are shown in Fig. 2(d). All compositions exhibit the typical layered morphology characteristic of MAX phases. However, noticeable microstructural evolution occurs with increasing nitrogen content. The particles gradually become more densely agglomerated, accompanied by an increase in surface roughness and morphological complexity. Meanwhile, the pore structure and exposed surface area undergo significant changes. These microstructural variations are likely associated with differences in crystal growth behavior, atomic rearrangement, and lattice distortion induced by C/N substitution. Such changes may alter interfacial characteristics and defect distributions, thereby affecting the dielectric polarization behavior and electromagnetic wave attenuation performance of the MAX phase.

The formation of $V_2GaC_{1-x}N_x$ solid-solution MAX phases was further verified by TEM, HRSTEM, and EDS. As shown in Fig. 3(a)-3(f), TEM-EDS elemental mapping reveals a homogeneous spatial distribution of V, Ga, C, and N throughout the particles for N0, N25, N50, N75, and N100, confirming the successful incorporation of nitrogen into the MAX-phase lattice without obvious elemental segregation. The uniform elemental distribution further supports the formation of a homogeneous solid solution. Figure 3(g) displays the HRSTEM-HAADF image of the V_2GaN MAX phase viewed along the $[1\bar{2}00]$ zone axis. Owing to the Z-contrast imaging mechanism, the heavier Ga atomic layers appear significantly brighter than the adjacent V-containing layers, whereas the lighter N atoms exhibit relatively weak contrast [32]. The image clearly reveals the characteristic layered structure of the MAX phase, consisting of alternating single Ga atomic layers and V_2N slabs stacked along the crystallographic c -axis. Furthermore, the zigzag arrangement of the V_6N octahedral units is distinctly observed, which is consistent with the atomic configurations reported for other M_2AX MAX phases. The well-resolved atomic columns and ordered stacking sequence confirm the high crystallinity of the synthesized V_2GaN phase and provide direct atomic-scale evidence for the successful formation of the layered MAX-phase structure.

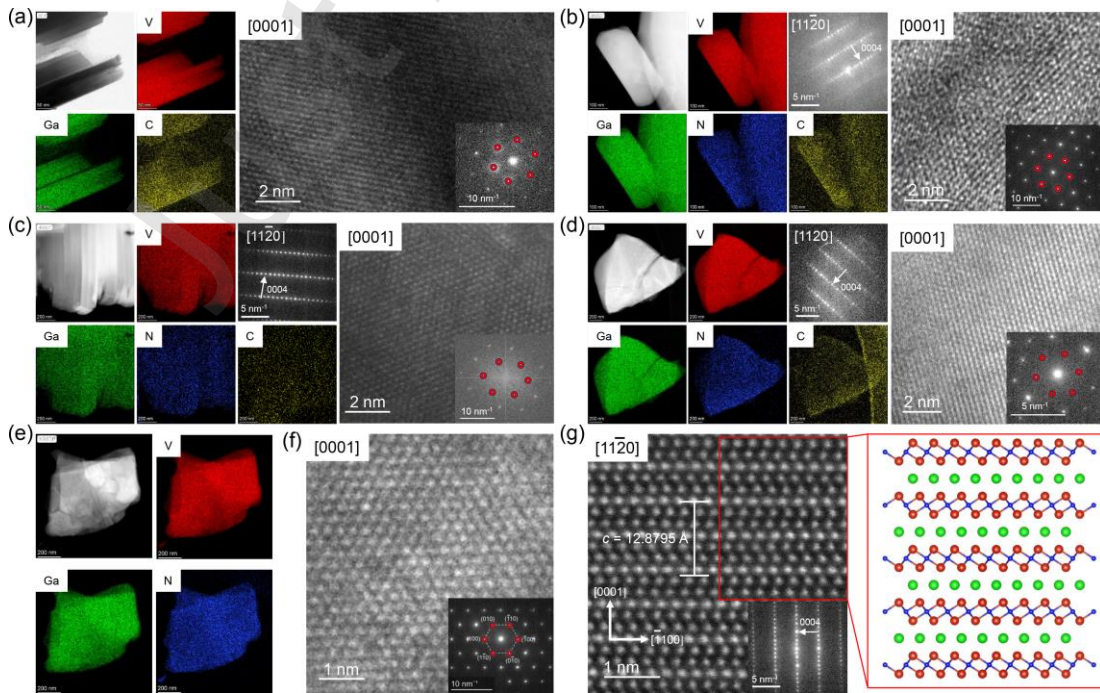


Fig. 3 Microstructures of $V_2GaC_{1-x}N_x$ MAX phases. HRTEM image (with inset showing selected

area electron diffraction pattern) and TEM mapping for N0 (a), N25 (b), N50 (c), N75 (d), and N100 (e, f) samples. The high-resolution high-angle annular dark-field scanning transmission electron microscopy (HRSTEM-HAADF) image of V_2GaN showing atomic positions along a $[1200]$ zone axis, and the red, green, and blue balls represent atoms in the M-, A-, and X-sites, respectively.

XPS was employed to investigate the local chemical environments and electronic structure evolution of the $V_2GaC_{1-x}N_x$ MAX phases. As a powerful surface-sensitive technique, XPS provides direct insight into bonding configurations and charge-transfer behavior, thereby enabling a detailed understanding of the compositional effects induced by C/N substitution. To elucidate the influence of nitrogen incorporation on the atomic-scale electronic structure, high-resolution spectra of the V $2p$, Ga $2p$, C $1s$, and N $1s$ core levels were collected for V_2GaC , $V_2GaC_{0.5}N_{0.5}$, and V_2GaN , as shown in Fig. 4. The deconvoluted V $2p$ spectra (Fig. 4(a)) reveal the evolution of the local coordination environment surrounding V atoms upon nitrogen substitution. For V_2GaC , the dominant component is attributed to V–C bonding, together with a minor V–O contribution arising from surface oxidation, which is commonly observed in MAX phases exposed to ambient conditions [27, 33]. Upon partial substitution of carbon by nitrogen, the V–C feature gradually evolves into mixed V–C/N coordination states in $V_2GaC_{0.5}N_{0.5}$, indicating the coexistence of V–C and V–N interactions. In V_2GaN , the spectrum is predominantly composed of V–N and V–O components, reflecting the complete replacement of carbon by nitrogen within the lattice [27]. Notably, the binding energies of the V-related components exhibit a systematic positive shift with increasing nitrogen content. This behavior suggests a gradual redistribution of electron density around the V atoms and indicates enhanced charge transfer resulting from the stronger electronegativity of nitrogen compared with carbon. The continuous evolution from V–C to V–C/N and finally to V–N bonding environments provides direct spectroscopic evidence for the successful formation of $V_2GaC_{1-x}N_x$ solid-solution phases.

Further insight into the electronic modulation induced by nitrogen incorporation is provided by the Ga $2p$ spectra (Fig. 4(b)). The spectra can be deconvoluted into Ga–V and Ga–O bonding components [18]. As the nitrogen concentration increases, the

Ga–O peak progressively shifts toward higher binding energies, indicating that the electronic environment of Ga atoms is also influenced by the substitution occurring at the X-site. Such behavior suggests that nitrogen incorporation induces long-range electronic redistribution throughout the MAX-phase lattice rather than affecting only the immediate V–X bonding region. The C 1s spectra of V_2GaC and $V_2GaC_{0.5}N_{0.5}$ are shown in Figs. 4(c)–4(d), respectively. A characteristic carbide-related C–V peak is observed at approximately 282.3–282.8 eV, confirming the presence of carbon bonded to vanadium within the MAX-phase framework [23]. In addition, both samples exhibit peaks centered at approximately 286.3 eV and 288.7 eV, corresponding to C–O and C=O species [23], respectively, which originate from surface oxidation and adsorbed oxygen-containing groups. The persistence of the carbide-related peak in $V_2GaC_{0.5}N_{0.5}$ indicates that carbon remains partially incorporated within the lattice after nitrogen substitution.

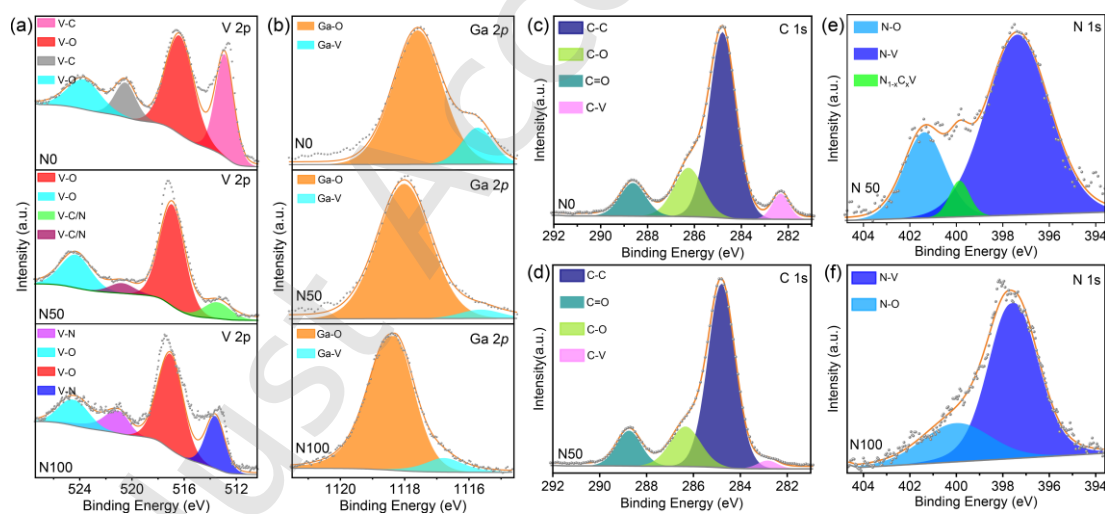


Fig. 4 High-resolution XPS spectra of V 2p for N0, N50, and N100 samples (a), Ga 2p for N0, N50, and N100 samples (b), C 1s for N0 (c) and N50 (d), and N 1s for N50 (e) and N100 (f).

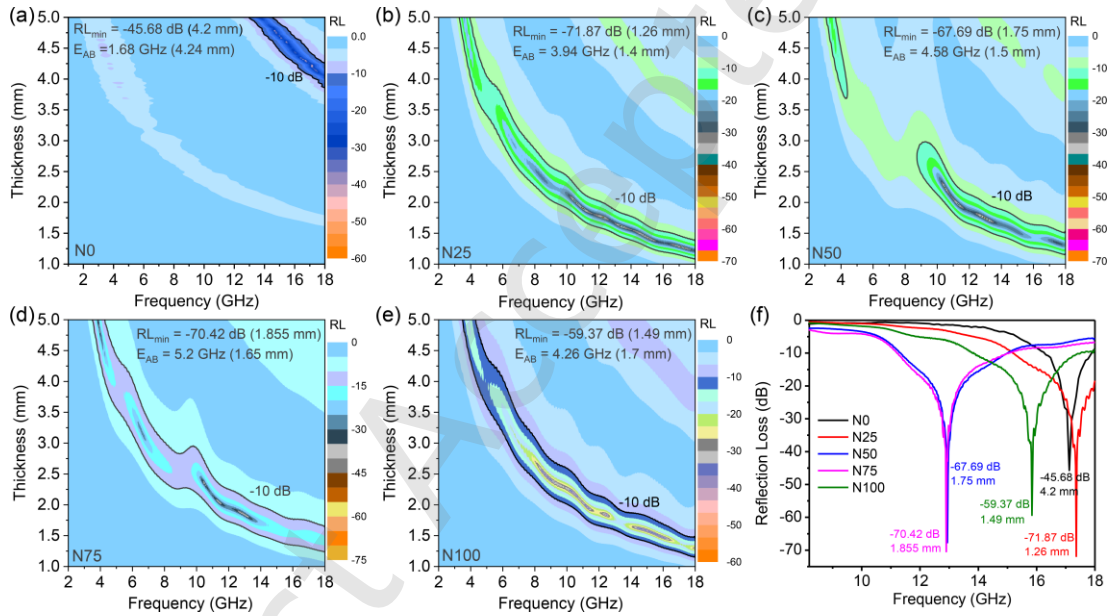
The N 1s spectra further verify the successful incorporation of nitrogen into the crystal structure. As shown in Fig. 4(e), $V_2GaC_{0.5}N_{0.5}$ exhibits a pronounced V–N peak centered at approximately 397.2 eV, accompanied by weaker N–O and VC_xN_{1-x} related components at higher binding energies [27]. In the fully nitrided V_2GaN phase (Fig. 4(f)), the V–N peak becomes substantially stronger and dominates the entire spectrum, confirming the establishment of a nitrogen-rich coordination environment. The gradual

enhancement of the V–N signal with increasing nitrogen content is highly consistent with the evolution observed in the V 2*p* spectra and provides strong evidence for the progressive substitution of carbon by nitrogen within the X-site atomic layers. Overall, the XPS results reveal that nitrogen incorporation significantly modifies the local bonding configuration and electronic structure of the V₂GaC_{1-x}N_x system. The observed binding-energy shifts and evolution of chemical bonding indicate enhanced charge transfer and stronger V–N interactions compared with V–C bonds. These findings are in excellent agreement with the DFT-calculated charge-density distributions and density-of-states analyses, which demonstrated increased electron localization and strengthened orbital hybridization following nitrogen substitution. Such electronic structure modulation is expected to facilitate charge transport, interfacial polarization, and dipolar relaxation processes, thereby providing a favorable foundation for enhanced electromagnetic-wave attenuation performance.

3.3 EM Wave Absorption Performance

Reflection loss and effective absorption bandwidth are widely employed to evaluate the electromagnetic wave absorption performance of microwave absorbers. The RL contour maps and corresponding EAB values of the V₂GaC_{1-x}N_x ($x = 0, 0.25, 0.5, 0.75$, and 1) MAX phases are presented in Fig. 5. As shown in Fig. 5(a), pristine V₂GaC exhibits an RL_{min} of approximately –45.68 dB at a thickness of 4.2 mm (Fig. 5a), indicating relatively limited absorption capability. Remarkably, the introduction of nitrogen significantly enhances the microwave absorption performance of the MAX phases. For V₂GaC_{0.75}N_{0.25}, V₂GaC_{0.5}N_{0.5}, V₂GaC_{0.25}N_{0.75}, and V₂GaN, the RL_{min} values reach –71.87 dB (1.26 mm), –67.69 dB (1.75 mm), –70.42 dB (1.855 mm), and –59.37 dB (1.549 mm) for $x = 0.25, 0.5, 0.75$, and 1, respectively, while the corresponding EAB values are 3.94, 4.58, 5.20, and 4.26 GHz (Figs. 5(b)–5(e)). Compared to V₂GaC, all nitrogen-containing compositions exhibit substantially enhanced absorption intensity and broadened effective absorption bandwidths (Fig. 5(f)). In particular, V₂GaC_{0.75}N_{0.25} achieves an ultralow RL_{min} of –71.87 dB at an ultrathin thickness of 1.26 mm (Fig. 5(b)), demonstrating outstanding attenuation

capability under lightweight design conditions. Moreover, the $V_2GaC_{0.5}N_{0.5}$, $V_2GaC_{0.25}N_{0.75}$, and V_2GaN samples exhibit pronounced frequency-modulation behavior, where the absorption peaks gradually shift toward lower frequencies with increasing absorber thickness. More importantly, the absorption regions with $RL < -10$ dB continuously cover the entire 2–18 GHz frequency range within the thickness interval of 1–5 mm, indicating excellent broadband absorption capability. Among all compositions, $V_2GaC_{0.25}N_{0.75}$ delivers the widest EAB of 5.20 GHz (12.8–18.0 GHz) at a thickness of only 1.65 mm. The remarkable enhancement in EMW absorption performance can be attributed to the synergistic effects induced by nitrogen substitution.



The enhanced EMW absorption is ascribed to nitrogen substitution, which reinforces V–X bonding, charge redistribution, and V 3d–N 2p hybridization, collectively accelerating charge transport, and polarization relaxation for excellent electromagnetic-to-thermal energy conversion.

Fig. 5 Electromagnetic wave absorption performance of $V_2GaC_{1-x}N_x$ MAX phases. The 2D representations of RL values with different thicknesses and frequencies for N0 (a), N25 (b), N50 (c), N75 (d), and N100 (e) samples, respectively. (f) Comparison of EM wave absorption properties among $V_2GaC_{1-x}N_x$ MAX phases.

Theoretical calculation (Fig. 1) reveals that for V_2GaN formed via N-for-C substitution at the X-site, high-strength V–N bonds stabilize the VN sublattice skeleton and increase the reaction energy barrier against oxygen-driven crystal degradation,

conferring excellent high-temperature oxidation resistance to the V_2GaN . This observation agrees with literature reports that N-containing MAX phases exhibit superior oxidation resistance relative to their C-based MAX-phase counterparts[34]. Although the intrinsic microwave-absorption performance of V_2GaN is not the optimum within the V_2GaN solid-solution family, it still shows considerable comprehensive electromagnetic-loss capacity compared with documented MAX-phase-based microwave-absorbing materials. Balancing its intrinsic oxidation-resistance merits and electromagnetic-loss properties, this work selects V_2GaN to decipher its microstructural-evolution mechanism under high-temperature oxidation and quantitatively assess the microwave-absorption performance of post-oxidized specimens. To assess its feasibility for high-temperature electromagnetic-protection applications, its high-temperature oxidation stability was characterized via TGA-DSC under a flowing-air atmosphere. As shown in Fig. 6(a), the TG curve (blue line) remains nearly stable below approximately 500 °C, with only a slight variation in mass, indicating excellent oxidation resistance within this temperature range and is superior to that reported for V_2GaC [35]. When the temperature increases to approximately 500-600 °C, the TG curve exhibits a pronounced and rapid mass increase indicating the onset of significant oxidation. With further increasing temperature, the mass of V_2GaN continues to increase and gradually reaches a plateau at approximately 800-850 °C, eventually leading to the formation of oxidation products such as V_2O_5 and vanadium nitride derivatives [35], corresponding to a final mass gain of approximately 45.4 wt%. The DTG (red line) curve further reveals a pronounced oxidation-rate peak at 630.6 °C, indicating that the oxidation reaction reaches its maximum rate near this temperature. Meanwhile, a distinct thermal event appears in the DSC (purple line) curve at approximately 630.3 °C, which closely coincides with the DTG peak, further confirming that this thermal event is primarily associated with the rapid oxidation process. Overall, the DTG-DSC results indicate that the material maintains good oxidation stability below approximately 500 °C, begins to undergo significant oxidation above approximately 550 °C, reaches its maximum oxidation rate at around

630 °C, and subsequently approaches completion of the oxidation process. Notably, the TG curve exhibits a slight decrease above 850 °C, which may be associated with the volatilization, decomposition, or phase transformation of certain oxidation products at elevated temperatures. The XRD results shown in Fig. 6(b) are consistent with the thermogravimetric analysis. Samples oxidized below 600 °C retain diffraction patterns nearly identical to those of the pristine material, confirming the preservation of the MAX-phase structure. In contrast, new diffraction peaks associated with V_2O_5 and V_2N emerge after oxidation at 650 °C, indicating the onset of structural decomposition. The excellent agreement between the TGA-DSC and XRD results confirms that $V_2\text{GaN}$ maintains structural integrity below 600 °C and undergoes significant phase transformation only at higher temperatures.

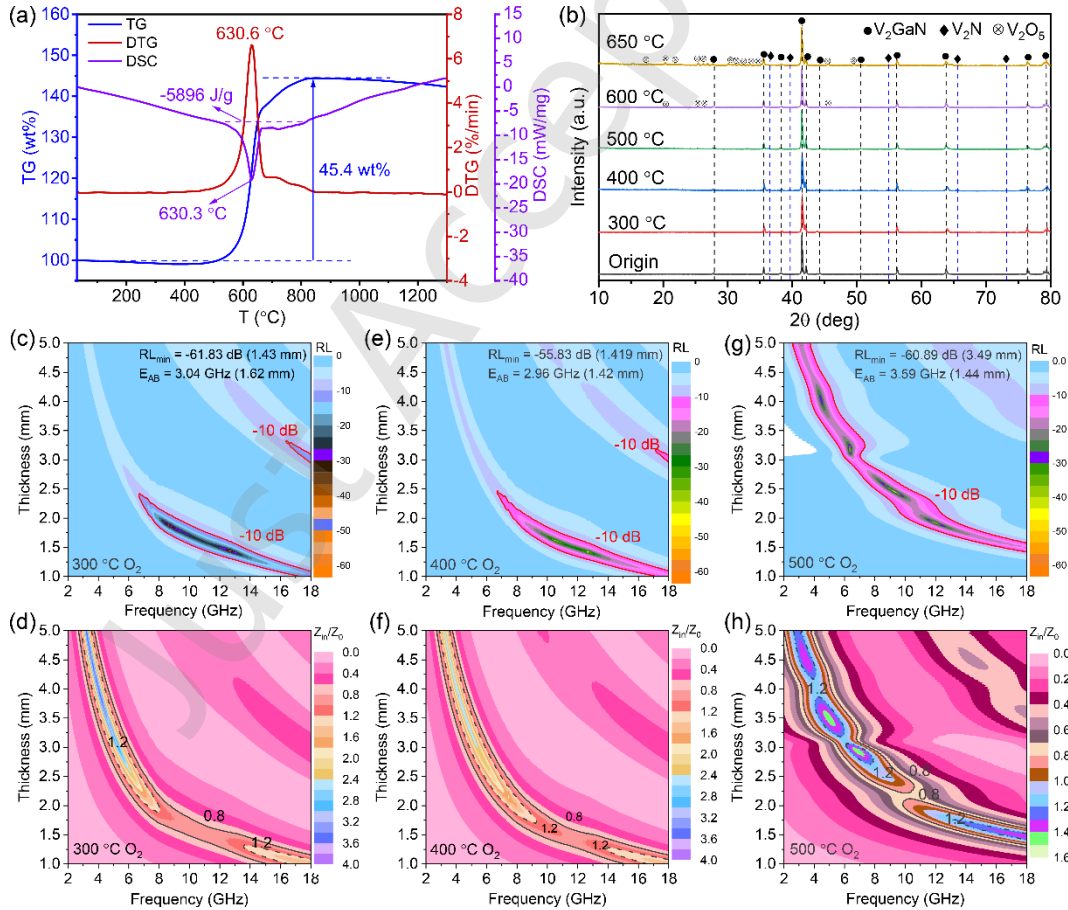


Fig. 6 (a) TGA-DTG-DSC curves of $V_2\text{GaN}$ from room temperature to 1300 °C in the air with a heating rate of 10 K min⁻¹. (b) XRD patterns of $V_2\text{GaN}$ after high-temperature treatment at 300 °C, 400 °C, 500 °C, 600 °C and 650 °C under air atmosphere, respectively. The frequency dependence of RL values at different thicknesses and the 2D representations of RL values with different thicknesses and frequencies for 300 °C (c, d), 400 °C (e, f) and 500 °C (g, h) oxidation samples,

respectively.

To further investigate the electromagnetic response of V_2GaN after high-temperature oxidation treatment, samples treatments at 300, 400, and 500 °C were selected for a systematic investigation of their RL and impedance-matching characteristics (Figs. 6(c)–6(h)). Notably, all samples maintain strong microwave absorption performance after oxidation. The sample subjected to 300 °C oxidation pretreatment exhibits an RL_{min} of -61.83 dB at 1.43 mm and an EAB of 3.04 GHz at 1.62 mm (Figs. 6(c-d)). For the sample treated at 400 °C, the RL_{min} slightly decreases to -55.83 dB at 1.42 mm, accompanied by an EAB of 2.96 GHz (Figs. 6(e-f)), whereas the specimen oxidized at 500 °C shows an RL_{min} of -60.89 dB at 3.49 mm and an EAB of 3.59 GHz (Figs. 6(g-h)). These results indicate that, following thermal treatment at different temperature, V_2GaN can largely remain its electromagnetic wave absorption performance after cooling to room temperature, provide that no significant structural degradation occurs. The slight fluctuations in absorption performance suggest that moderate oxidation primarily alters the local electronic environment and defect distribution rather than inducing catastrophic changes in crystal structure. The impedance-matching maps provide further insight into the underlying absorption mechanism. As shown in Figs. 6(d) and 6(f), the impedance-matching regions ($Z_{in}/Z_0 \approx 1$) of the samples thermally treated at 300 and 400 °C are mainly concentrated in the low-frequency and thin-thickness regions, indicating similar electromagnetic parameter distributions and absorption mechanisms. The limited variation in both RL and EAB further suggests that mild oxidation has only a minor influence on the intrinsic dielectric and magnetic responses of the material. Meanwhile, the limited variations in both RL and EAB further demonstrate that mild oxidation at 300–400 °C has only a minor influence on the intrinsic electromagnetic response of V_2GaN under subsequent room-temperature measurement conditions. In contrast, the sample oxidized at 500 °C exhibits a substantially broader impedance-matching region (Fig. 6(h)), spanning a wider frequency–thickness space and displaying reduced impedance fluctuations. This behavior indicates that oxidation at a high-temperature induces more pronounced

microstructural and dielectric-state modifications, thereby regulating the dielectric response and enabling the thermally treated sample to achieve across a broader impedance-matching range under subsequent room-temperature testing conditions. Although a greater absorber thickness is required to achieve optimal performance, the broadened matching region is advantageous for broadband microwave absorption applications. Overall, V_2GaN retains a high level of electromagnetic wave absorption performance after high-temperature treatment followed by cooling to room temperature, demonstrating its robust structural integrity and functional retention upon thermal exposure.

3.4 EM Wave Absorption Mechanism

To elucidate the electromagnetic wave absorption mechanism of the $V_2GaC_{1-x}N_x$ MAX phases, the frequency-dependent electromagnetic parameters, including the complex permittivity ($\epsilon_r = \epsilon' + j\epsilon''$) and complex permeability ($\mu_r = \mu' + j\mu''$), were systematically investigated. Since $V_2GaC_{1-x}N_x$ exhibits non-ferromagnetic behavior at room temperature ($\mu' = 1$, $\mu'' = 0$), magnetic loss can be neglected and the EMW absorption performance is primarily governed by dielectric loss mechanisms. In this context, the real part of permittivity (ϵ') reflects the capability of storing electromagnetic energy, whereas the imaginary part (ϵ'') represents the ability to dissipate electromagnetic energy [24]. The frequency-dependent permittivity spectra of $V_2GaC_{1-x}N_x$ ($x = 0, 0.25, 0.5, 0.75$, and 1) are shown in Fig. 7(a)-7(b), respectively. Among all compositions, $V_2GaC_{0.5}N_{0.5}$ exhibits the highest ϵ' (15.29–22.42) and ϵ'' (8.25–11.28) within the low-frequency region (2–7 GHz). In contrast, $V_2GaC_{0.75}N_{0.25}$ displays the highest ϵ' (12.68–14.44) values in the X- and Ku-band regions (8–18 GHz), suggesting enhanced dielectric response at higher frequencies [36]. Moreover, distinct dielectric resonance peaks are observed throughout the measured frequency range, indicating the presence of multiple polarization-relaxation processes. These dielectric resonances can be attributed to the combined effects of dipolar polarization and interfacial polarization [37]. DFT and XPS analyses collectively demonstrate that nitrogen substitution triggers significant charge redistribution and tailors the local

electronic structure via strengthened V–N interactions and V $3d$ –N $2p$ hybridization. The asymmetric charge distribution thus created gives rise to abundant polarization centers. Meanwhile, the lattice distortion and compositional fluctuations induced by C/N solid solution formation introduce extra heterogeneous interfaces, collectively resulting in a marked enhancement of polarization relaxation.

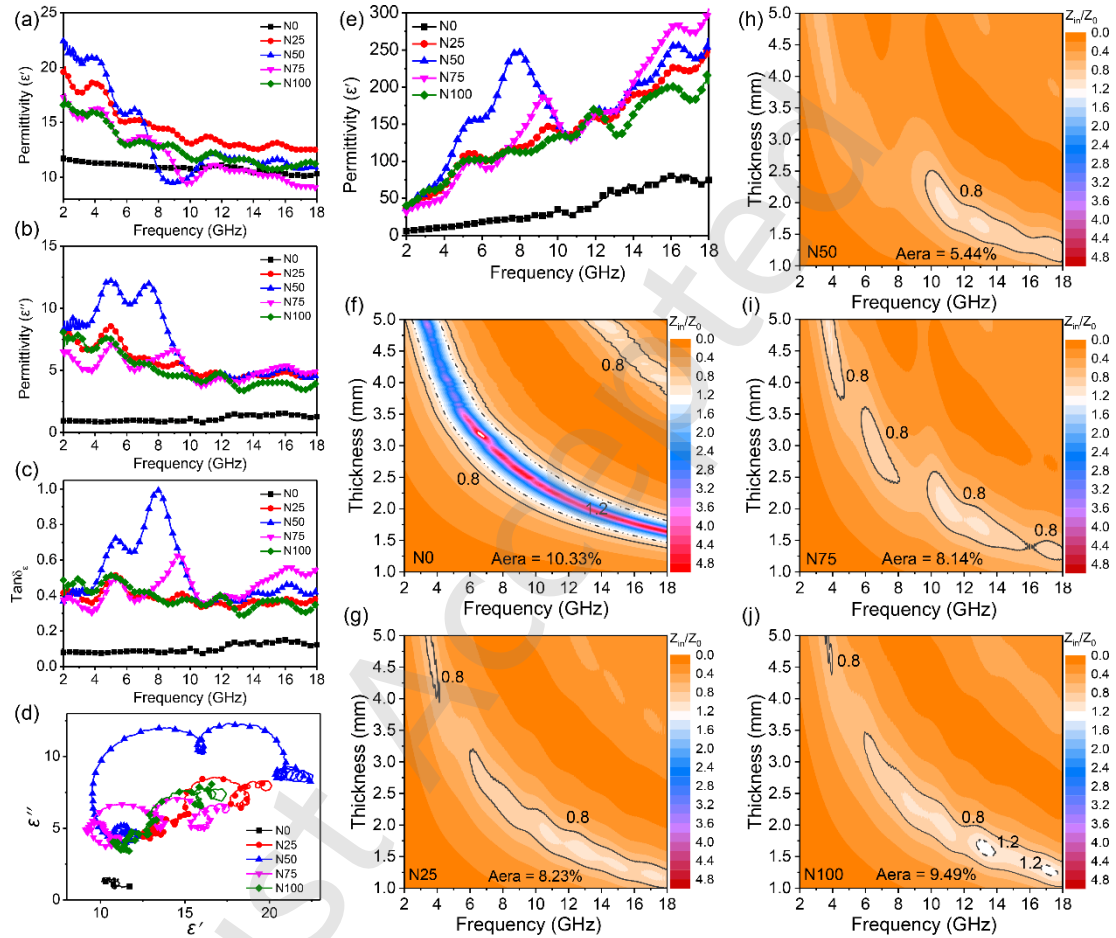


Fig. 7 EM parameters of $V_2GaC_{1-x}N_x$ MAX phases. The real permittivity (a), imaginary permittivity (b), tangent loss (c), Cole-Cole semicircles (d), and attenuation constants (e) as a function of frequency for N0, N25, N50, N75, and N100 samples, respectively. The frequency dependence of impedance matching (Z_{in}/Z_0) values at different thicknesses of N0 (f), N25 (g), N50 (h), N75 (i), and N100 (j) samples, respectively.

The dielectric loss tangent ($\tan \delta_\epsilon$) shown in Fig. 7(c) further confirms the enhanced dielectric dissipation capability of the nitrogen-containing compositions. To distinguish conductive loss from polarization loss, Cole–Cole plots were constructed according to Debye relaxation theory [38]. Multiple distorted semicircles are observed, indicating the coexistence of several polarization-relaxation processes. More importantly, a

pronounced straight-tail region appears in the low-frequency regime, suggesting significant conductive loss contributions. The depressed semicircles and elongated tail imply that C/N solid-solution engineering introduces additional scattering centers and interfacial defects, thereby enhancing polarization relaxation and charge-transfer processes (Fig. 7(d)). These results demonstrate that X-site compositional regulation effectively tailors the dielectric response of V-based MAX phases. Besides dielectric loss capability, efficient microwave absorption requires a balance between attenuation capacity and impedance matching. Fig. 7(e) presents the attenuation constants (α) of the $V_2GaC_{1-x}N_x$ series. Compared with pristine V_2GaC , all nitrogen-containing compositions exhibit significantly higher attenuation constants throughout the 2–18 GHz frequency range, indicating stronger electromagnetic energy dissipation capability [39]. This enhancement is attributed to the synergistic contributions of improved electrical conductivity, strengthened dipolar polarization, and increased interfacial polarization induced by nitrogen incorporation. However, a high attenuation constant alone cannot guarantee excellent microwave absorption performance because excessive dielectric loss often results in severe impedance mismatch between the absorber and free space. Therefore, quantitative analysis of the impedance matching ($0.8 \leq Z_{in}/Z_0 \leq 1.2$, which indicating minimal wave reflection [40, 41]) was further evaluated, as shown in Figs. 7(f)–7(j). The N0 sample exhibits the highest impedance-matching area ratio (10.33%), which facilitates electromagnetic-wave penetration; however, its relatively weak dielectric loss limits its absorption capability, requiring a relatively large thickness of 4.2 mm to achieve effective absorption. Upon N incorporation, the dielectric constant increases, enhancing polarization loss while simultaneously narrowing the impedance-matching window. For N25, the impedance-matching area ratio decreases to 8.23%, but the enhancement in loss capability becomes dominant, yielding a RL_{min} of -71.87 dB and a substantially reduced matching thickness. With further increasing N content to N50, the impedance-matching area ratio decreases to the lowest value of 5.44%, while the excessively high dielectric constant aggravates interfacial reflection. Nevertheless, the strong dielectric loss still enables an RL_{min} of

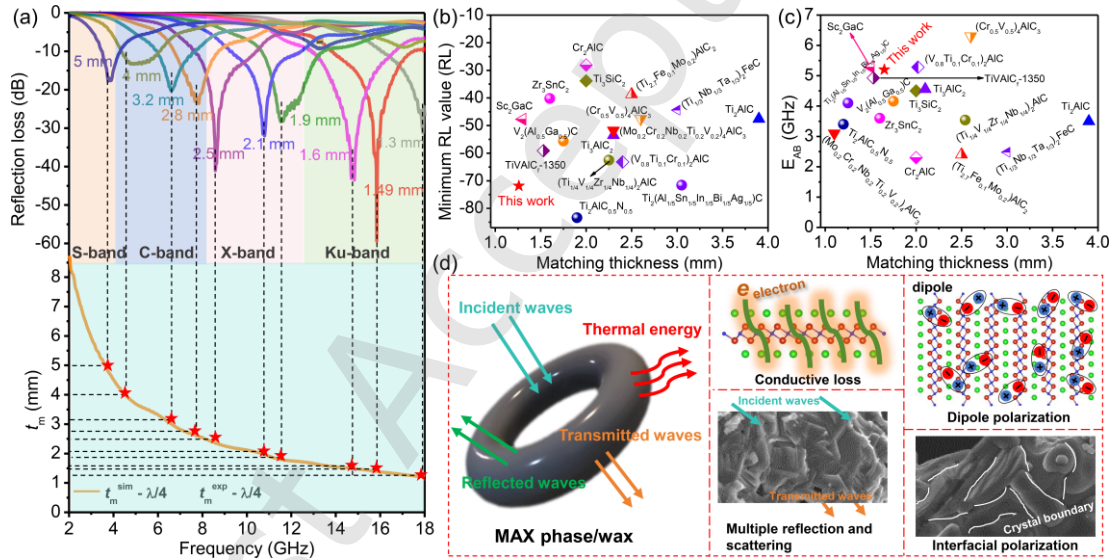
−67.69 dB and an EAB of 4.58 GHz within the limited impedance-matched region, although its high-performance absorption window is substantially narrowed. As the N content is further increased, the impedance-matching area ratios of N75 and N100 recover to 8.14% and 9.49%, respectively. Among them, N75 achieves the optimal balance between impedance matching and attenuation capability, delivering the maximum EAB of 5.20 GHz and thus the best overall microwave absorption performance. Overall, N incorporation induces a non-monotonic evolution of microwave absorption performance through the coupled regulation of impedance matching and electromagnetic loss, characterized by an initial enhancement, subsequent restriction, and eventual re-optimization.

To further clarify the absorption mechanism, the relationship between matching thickness and absorption peak frequency was analyzed according to the quarter-wavelength cancellation model. As shown in Fig. 8(a), the experimental absorption peak frequencies shift progressively toward lower frequencies with increasing absorber thickness. The experimentally determined matching thicknesses agree well with the theoretical quarter-wavelength ($\lambda/4$) curve indicating that the dominant absorption mechanism follows the quarter-wavelength interference principle [42, 43]. Under this mechanism, destructive interference between incident and reflected waves effectively minimizes surface reflection and promotes electromagnetic energy dissipation within the absorber. Figs. 8(b)-8(c) compare the microwave absorption performance of the present materials with previously reported MAX-phase absorbers. Several important observations can be drawn. First, $\text{V}_2\text{GaC}_{0.75}\text{N}_{0.25}$ exhibits the most outstanding microwave absorption performance among currently reported V-based and Ga-based MAX phases. Second, effective absorption ($\text{RL} < -10$ dB), corresponding to more than 90% attenuation of incident electromagnetic energy, can be achieved across the S, C, X, and Ku bands using absorber thicknesses ranging from only 1.3 to 5 mm. Third, V_2GaN retains excellent microwave absorption capability even after oxidation treatment at 500 °C, demonstrating exceptional thermal reliability. Finally, compared with previously reported MAX-phase absorbers, including MAX-based composites,

magnetic MAX phases, and other solid-solution systems, the $V_2GaC_{1-x}N_x$ series exhibits a superior combination of strong attenuation, broad effective bandwidth, and reduced matching thickness. Particularly noteworthy is that the RL_{min} of $V_2GaC_{0.75}N_{0.25}$ approaches that of the best-performing $Ti_2AlC_{0.5}N_{0.5}$ system reported to date, while simultaneously offering advantages in both matching thickness and effective absorption bandwidth. These results clearly demonstrate the effectiveness of X-site nitrogen engineering as a strategy for enhancing the microwave absorption performance of MAX phases. Combined with their intrinsic layered structure, excellent oxidation resistance, and high-temperature stability, $V_2GaC_{1-x}N_x$ MAX phases represent promising candidates for electromagnetic protection applications in aerospace, military, electronic, and harsh-environment technologies.

A schematic illustration of the microwave absorption mechanism is presented in Fig. 8(d). X-site N substitution for C serves as the intrinsic driving force for regulating the electronic structure and microwave absorption performance of $V_2GaC_{1-x}N_x$ MAX phases. Theoretical calculations reveal that N incorporation substantially reconstructs the V-3d orbitals and, owing to the strong electronegativity of N, induces charge transfer from V to N, thereby generating more polar V–N bonds and pronounced local charge asymmetry[44]. This electronic-structure reconstruction exerts a dual regulatory effect. On the one hand, N substitution modifies the carrier distribution and transport behavior near the Fermi level, thereby regulating conduction loss. On the other hand, the local charge asymmetry induced by V–N bonding generates abundant intrinsic dipolar polarization centers, which undergo dipolar relaxation under an alternating electromagnetic field, significantly enhancing dielectric polarization loss. Experimental results further demonstrate that as the N content increases from N25 to N50, the V–N-bond-induced polarization effect is progressively strengthened, leading to markedly enhanced dielectric loss and EMW attenuation. With further increasing N content to N75 and N100, the continuously reconstructed electronic structure re-regulates the dielectric response, partially restoring impedance matching while retaining substantial polarization loss. Notably, N75 achieves the optimal synergy between impedance

matching and electromagnetic loss, delivering a maximum effective absorption bandwidth of 5.2 GHz. Thus, X-site N engineering establishes an intrinsic “bonding reconstruction–charge transfer–polarization enhancement–dielectric response regulation” pathway, which further coordinates the competition between impedance matching and electromagnetic loss and gives rise to the characteristic evolution of “loss enhancement–matching limitation–synergistic re-optimization.” Beyond the regulation of the intrinsic dielectric response, the rough layered morphology facilitates multiple reflection and scattering of electromagnetic waves, thereby prolonging their propagation paths and increasing the probability of energy dissipation[45, 46]. Meanwhile, the minor VN and V₂N impurity phases may provide auxiliary attenuation



through modulation of the local dielectric environment and interfacial polarization at heterogeneous interfaces. The synergistic contribution of intrinsic electronic-structure regulation and structural/interfacial effects ultimately endows V₂GaC_{1-x}N_x MAX phases with excellent EMW attenuation capability.

Fig. 8 (a) Frequency-dependent RL and simulations of the t_m versus f_m under the $\lambda/4$ model for the V₂GaN sample, the pentacle represents the experimental t_m (written as t_m^{exp}). (b-c) Comparison of EM wave absorption properties among V₂GaN MAX phase, please refer to Table 1. (d) Schematic illustration of microwave absorption mechanisms and polarization model for V₂GaN MAX phase.

To evaluate the practical electromagnetic stealth capability of the V₂GaC_{1-x}N_x MAX phases, three-dimensional radar cross-section (RCS) simulations were performed. The corresponding two-dimensional RCS distributions as a function of polar angle (θ)

are presented in Figs. 9(a)–9(f). As expected, the bare perfect electric conductor (PEC) exhibits the strongest scattering response, characterized by high RCS values over the entire angular range [47]. After coating with the $V_2GaC_{1-x}N_x$ absorbers, the scattering intensity is significantly suppressed, demonstrating the effectiveness of these materials in mitigating electromagnetic reflection. Notably, the overall RCS amplitude decreases substantially with the introduction of nitrogen, indicating enhanced electromagnetic attenuation and scattering suppression. The reduction is particularly pronounced in the vicinity of $\theta = 0^\circ$, corresponding to the main forward-scattering lobe. This behavior suggests that nitrogen incorporation effectively weakens the reflection of normally incident electromagnetic waves, thereby improving the stealth performance of the coated PEC surface. Among all investigated compositions, the N25 sample exhibits the lowest overall RCS level (Fig. 9(g)), which is consistent with its superior reflection-loss performance and optimized impedance-matching characteristics. The excellent agreement between the RCS simulations and microwave absorption measurements confirms that the enhanced attenuation capability achieved through X-site nitrogen regulation can be effectively translated into reduced electromagnetic scattering.

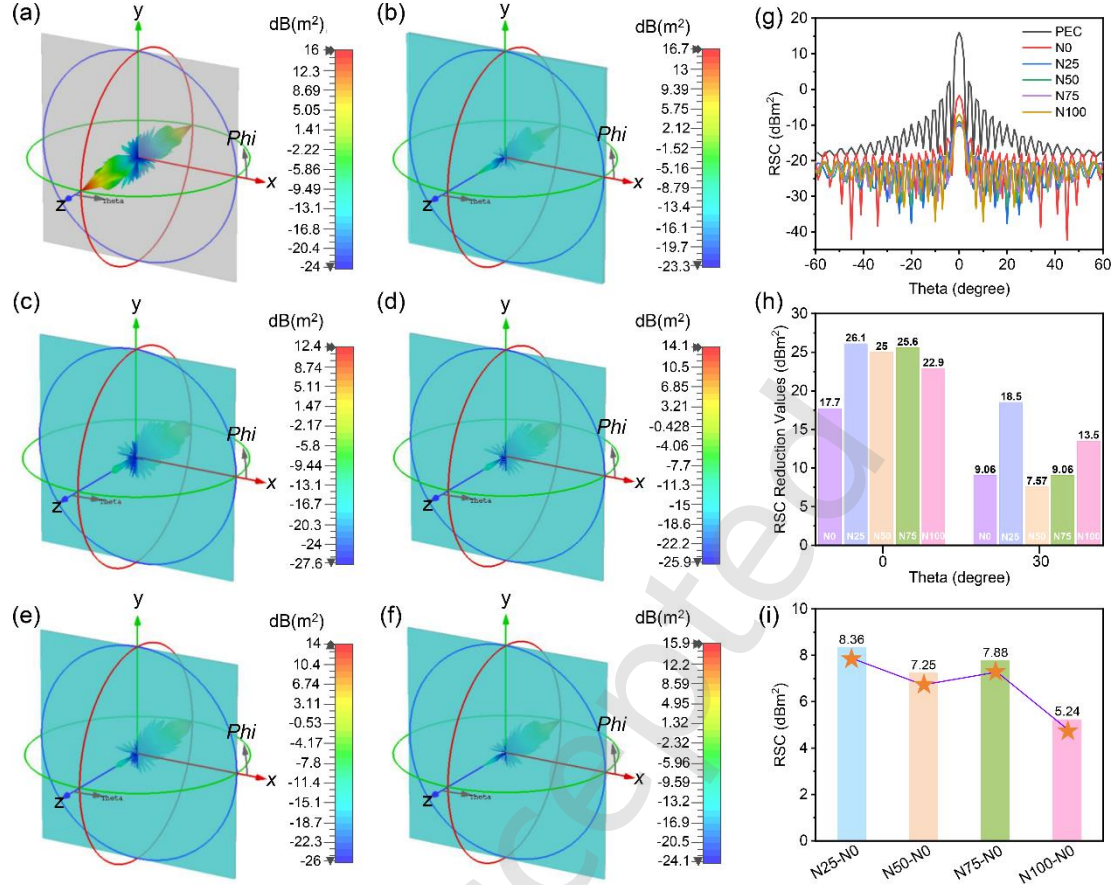


Fig. 9 3D RCS plot for the PEC substrate covered with different absorbing materials, (a) PEC, (b) N0, (c) N25, (d) N50, (e) N75, and (f) N100. (g) 2D RCS curves of PEC, N0, N25, N50, N75, and N100. (h) RCS reduction values of N0, N25, N50, N75, and N100. (i) Compared with N0, the RCS reduction values of N25-N0, N50-N0, N75-N0, and N100-N0.

Figure 9(h) summarizes the RCS reduction values at observation angles of 0° and 30° . As the nitrogen content increases, the RCS reduction initially increases and subsequently reaches a plateau or exhibits a slight decline. For example, the maximum reductions reach 26.1 dBm² and 25.6 dBm² for the N50 and N75 samples, respectively. These results indicate that nitrogen incorporation effectively suppresses forward scattering, while excessive nitrogen addition provides diminishing improvements. This trend is consistent with the electromagnetic parameter analysis, where an optimal balance between attenuation capability and impedance matching is achieved at intermediate nitrogen concentrations rather than at the highest nitrogen content. To further assess the synergistic effects of material composition and structural design, the RCS differences between the composite configurations and the reference N0 structure were analyzed (Fig. 9(i)). The calculated reductions for N25-N0, N50-N0, N75-N0, and N100-N0.

and N100–N0 are 8.36, 7.25, 7.88, and 5.24 dBm², respectively. Although the reduction values exhibit a fluctuating trend, all composite configurations show lower RCS values than the reference structure, indicating that the integration of optimized absorber compositions with appropriate structural configurations can further enhance electromagnetic scattering suppression. In particular, the N100-based composite demonstrates the most pronounced structure-induced scattering reduction, highlighting the importance of structure–material synergy in practical stealth applications. Overall, the RCS simulations provide compelling evidence that X-site nitrogen engineering effectively reduces both the reflection and scattering of electromagnetic waves from PEC surfaces. Combined with the excellent reflection-loss performance, broad effective absorption bandwidth, and favorable impedance-matching characteristics, the V₂GaC_{1-x}N_x MAX phases exhibit considerable potential for advanced electromagnetic stealth, radar signature reduction, and high-performance electromagnetic protection applications.

Table 1. Microwave absorption properties of the nitrogen-substituted MAX phase and other MAX absorbing materials are presented here for comparison.

No.	Materials	Minimum RL		Optimum E _{AB}		Refs.
		Value (dB)	Thickness (mm)	Value (GHz)	Thickness (mm)	
1	Ti ₃ SiC ₂	-33.8	2	4.5	2	[15]
2	Ti ₃ AlC ₂	-53.48	2.3	4.56	2.1	[16]
3	Cr ₂ AlC	-28.1	2	2.3	2	[17]
4	Sc ₂ GaC	-47.7	1.3	5.28	1.5	[18]
5	(Cr _{0.5} V _{0.5}) ₄ AlC ₃	-47.6	2.6	6.3	2.3	[19]
6	(V _{0.6} Ti _{0.2} Cr _{0.2}) ₂ AlC	-56.2	1.75	4.16	1.75	[20]
7	Ti ₂ (Al _{1/5} Sn _{1/5} In _{1/5} Bi _{1/5} Ag _{1/5})C	-71.6	3.05	4.1	1.25	[22]
8	Ti ₂ AlC	-47.6	3.9	3.5	3.9	[48]
9	TiVAIC _{F-1350}	-59.13	1.53	4.93	1.53	[48]
10	Zr ₃ SnC ₂	-40.2	1.6	3.6	1.6	[49]
11	Ti _{2.7} Fe _{0.1} Mo _{0.2} AlC ₂	-38.7	2.5	2.4	2.5	[50]
12	(Ti _{1/3} Nb _{1/3} Ta _{1/3}) ₂ FeC	-44.4	3	2.48	3	[51]
13	(TaNbTiV) ₂ AlC	-43.83	1.6	3.485	1.6	[52]
14	(Mo _{0.2} Cr _{0.2} Nb _{0.2} Ti _{0.2} V _{0.2}) ₄ AlC ₃	-51.8	2.3	3.1	1.1	[53]
15	V ₂ (Al _{0.5} Ga _{0.5})C	-55.62	1.75	4.16	1.75	[54]
16	Ti ₂ AlC _{0.5} N _{0.5}	-83.4	1.9	3.4	1.2	[55]
17	SiC@Ti ₃ SiC ₂	-68.59	2.3	5.6	2.3	[56]

18	20 wt%0D/1D Cr ₂ GaC/C	-70.2	1.62	4.49	1.62	[57]
19	Carbon fiber@(V _{0.8} Ti _{0.1} Cr _{0.1}) ₂ AlC	-63.26	2.4	5.28	2.02	[58]
20	V ₂ GaC _{0.75} N _{0.25}	-71.87	1.26	3.94	1.4	This work
21	V ₂ GaC _{0.5} N _{0.5}	-67.69	1.75	4.58	1.5	This work
22	V ₂ GaC _{0.25} N _{0.75}	-70.42	1.855	5.2	1.65	This work
23	V ₂ GaN	-59.37	1.49	4.26	1.7	This work

4. Conclusions

In this work, a series of X-site solid-solution V₂GaC_{1-x}N_x MAX phases were successfully synthesized, and the effect of nitrogen incorporation on their electromagnetic wave absorption behavior was systematically investigated. Nitrogen substitution effectively regulated the electronic structure, dielectric response, and impedance matching of the V-based MAX phases, resulting in significantly enhanced microwave absorption performance. Among all compositions, V₂GaC_{0.75}N_{0.25} exhibited the best performance, achieving an ultralow RL_{min} of -71.87 dB at a matching thickness of only 1.26 mm, while V₂GaC_{0.25}N_{0.75} delivered the widest effective absorption bandwidth of 5.2 GHz. In addition, V₂GaN retained excellent absorption capability after oxidation treatment at 500 °C, which underscores its remarkable thermal stability of electromagnetic properties. The results demonstrate that the incorporation of N at the X site effectively regulates the V–N interactions and induces localized charge redistribution, thereby reconstructing the electronic structure and electromagnetic response characteristics of the MAX phase. This finding provides a new design strategy for the precise regulation of microwave absorption performance in MAX phases through X-site element engineering.

Declaration of competing interest

The authors declare no conflict of interest.

Data Availability Statement

Data will be made available on request.

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