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The synthesis and electrical transport properties of Carbon/Cr₂GaC MAX phase composite microwires

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Abstract. While MAX phases offer an exotic combination of ceramic and metallic properties, rendering them a unique class of materials, their applications remain virtually hypothetical. To overcome this shortcoming, a sol-gel based route is introduced that allows access to microwires in the range of tens of micrometers. Thorough structural characterization through XRD, SEM, EDS, and AFM demonstrates a successful synthesis of carbonaceous Cr₂GaC wires, and advanced low temperature electronic transport measurements revealed resistivity behavior dominated by amorphous carbon. The tunability of electronic behavior of the obtained microwires is shown by a halide post-synthesis treatment, allowing purposeful engineering of the microwires' electrical conductivity. Raman studies revealed the polyanionic nature of the intercalated halides and a slow decrease in halide concentration was concluded from time-dependent conductivity measurements. Based on these findings, the process is considered a viable candidate for fabricating chemiresistive halogen gas sensors.

Introduction. MAX phases are ternary transition metal-based carbides, nitrides and carbonitrides that crystallize in the hexagonal space group $P6_3/mmc$ with the general chemical formula of $M_{n+1}AX_n$ ($n = 1, 2, 3, 4$).^{1,2} M is an early transition metal, A mainly group 13 or 14 elements, and X is carbon and/or nitrogen. The M and X elements form octahedra (M_6X), that are intercalated with a single-atom layer of A . In so-called 211, 312 and 413 MAX phases, two, three and four layers of M alternate with one layer of the A element (indicated by n), respectively. Because of their unique crystalline structure and chemistry, MAX phases offer a combination of typical ceramic and metallic properties. Some examples for these are high thermal and electrical conductivity, chemical resistivity, oxidation resistance, damage tolerance, and fatigue resistance.¹ Recent studies have further predicted that these materials offer unique magnetic³ and quantum properties such as ferromagnetic ordering.⁴

Despite their traditional and exotic properties, MAX phases are typically prepared by solid state reaction techniques which yield the target compounds in powder or pelletized form.⁵⁻⁷ While these conventional methods are effective in producing MAX phases, they have their shortcomings especially for those compounds involving low melting point A atoms, such as Ga ($M_{n+1}GaX_n$). Achieving a homogenous or even decently mixed precursor mixture is shown to be a difficult task, for example for Ti₂GaC, Cr₂GaC, and Ti₄GaC₃.⁸ Furthermore, these solid state techniques present great challenges in achieving more sophisticated and complex morphologies extending well beyond 0D nanoparticles or pelletized blocks. Hence, despite the tremendous progress in the micro and nanostructure based studies on other layered material systems,⁹⁻¹¹ low dimensional MAX phases still remain experimentally unexplored. Electronic and other properties of a material critically hinge on its dimension. Fascinating properties arising from the quantum confinement in 1D and 2D structures are routinely exploited in miniaturized new-generation devices.^{12,13} Recently, 1D structures in the form of wires, rods

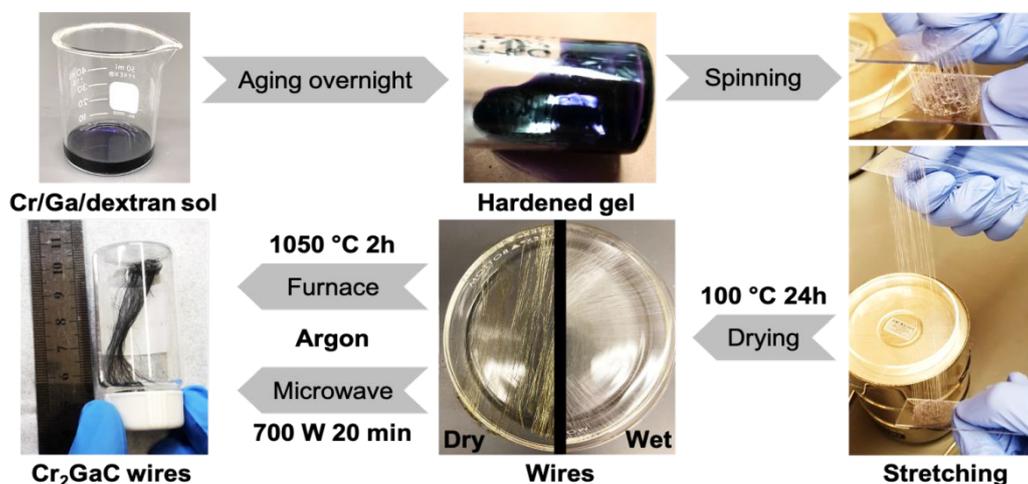


Figure 1: Schematic illustrating the process of preparing Cr₂GaC microwires from gel precursor (top left) to spun wires (right) by means of photographs. The bottom center shows the wires pre- and post-drying, and the bottom left shows the final product after annealing in Ar, either via conventional heating or microwave heating.

and ribbons have shown a great promise to be used as advanced catalysts,¹⁴ optical waveguides,^{15,16} and sensors¹⁷ due to their high aspect ratios. Enhanced surface area of 1D structures also adds another degree of freedom for tuning material properties by surface functionalization.¹⁸ Therefore, to completely explore the MAX phases at low dimensions, there is a need to generate 1D ribbon or wire-like structures for added functionalities and easy integration into electronics, optics, energy conversion, and even quantum technology related fields.^{19–21} Here, we report on the first demonstration of carbonaceous Cr_2GaC MAX phase microwires using sol-gel chemistry by both non-conventional microwave and conventional thermal heating techniques. This approach introduces a scalable sol-gel chemistry route to produce 1D carbonaceous Cr_2GaC MAX wires, offering a viable and versatile alternative to conventional methods. Cryogenic electronic transport measurements performed on these wires show that these microwires exhibit classical metallic, insulating-like, as well as a unique non-monotonic temperature dependence. Subsequent bromine and iodine halide treatment on these wires enables us to further reduce the electrical resistivity and time-resolved conductivity measurements offer fundamental insights into the halide treatment process.

Results and Discussion

A typical synthesis was based on 2.5 g of dextran (average molecular weight: 75k M, Alfa Aesar) dissolved in 2.5 mL deionized water containing the metal precursors. The metal precursors were $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Honeywell, 98%) and $\text{Ga}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (Alfa Aesar, 99.9%) and were weighed in air. The optimal concentration of the metal ion precursor solution was found to be 1.7 mmol/mL. This translates, for a 2.5 g dextran synthesis, into 1.1337 g of chromium nitrate and 0.4181 g of gallium nitrate, giving a Cr:Ga ration of 2:1. The precursors were dissolved in 2.5 mL DI water prior to adding 2.5 g of dextran, which was stirred in once the metal precursors were entirely dissolved. Upon complete incorporation of dextran, the as-obtained, viscous, deep-violet solution was rested overnight at room temperature. This process resulted in a slightly hardened and sticky gel, which subsequently was used to spin wires, using two glass microscopy slides. A small amount of gel was applied to a slide and spread out using the second slide by applying firm pressure. Pulling the slides apart quickly resulted in spontaneous formation of multiple wires, which, depending on the amount used, could be easily pulled into lengths greater than one meter. The wires were stretched over a petri dish and dried overnight at 100 °C. After drying, the wires changed color from a violet hue to a brownish yellow. Using an alumina crucible, the wires were heated under flowing argon with a heating rate of 2 °C/min to 1050 °C, and held at that temperature for 2 hours before cooling to room temperature (tube furnace EST, Carbolite).

In case of microwave assisted synthesis, a setup similar to previously reported works has been used,^{22,23} with a modification allowing to run Ar into the reaction chamber during the heating process. A quartz tube was used to guide argon into the reaction through an opening in the top of the microwave housing. Wires combusted in the setup were placed in an alumina tube, which was evacuated and flushed with Ar three times, embedded in 7 g of graphite granules (activated charcoal, DARCO, 12-20 mesh, Honeywell) in the insulation housing (alumina fiber boards, Skyline Components LLC), and flushed for 15 minutes prior to heating it under flowing Ar (0.25 LPM). The microwave (Mars 6, CEM Corporation) was set to 700 W and was run for 20 minutes. A sample preparation scheme is illustrated in Figure 1.

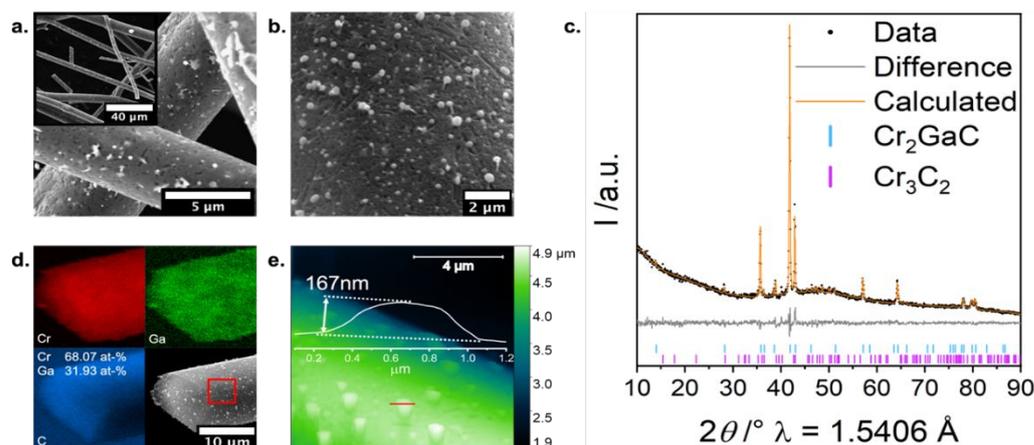


Figure 2: **a.** SEM micrograph showing multiple wires. Inset showing an overview micrograph demonstrating the variance in diameter. **b.** SEM micrograph showing the surface morphology of the furnace-derived microwires; **c.** Rietveld refinement of furnace-derived Cr_2GaC XRD data, fitted with structural models of Cr_2GaC and Cr_3C_2 ; **d.** SEM EDS elemental analysis showing the uniform distribution of Cr, Ga, and C, as well as the expected 2:1 ratio of Cr:Ga; **e.** AFM data (10 x 10 μm) showing the surface depositions as well as an extracted profile (red line, profile overlaid in white), with the determined height of 167 nm.

Structural understanding of 1D MAX wires

The process, outlined above, produced Cr_2GaC MAX phase wires with well-rounded curvatures and diameters ranging from a few to tens of micrometers as shown in the SEM images in Figure 2a and Figure 3a. As-synthesized wires were structurally characterized using laboratory-scale X-ray powder diffraction (D2 Phaser 2nd Generation, Bruker), and to minimize anisotropic effects as much as possible, the samples were ground into a powder using an agate mortar. All data were refined using the Rietveld method and Topas.²⁴ Both synthesis strategies resulted in mainly Cr_2GaC wires, with Cr_3C_2 as the dominant side phase (6 – 14 wt-%). Interestingly, furnace wire samples exhibit a more amorphous character compared to microwave wires, clearly visible in the higher noise level in Figure 2c compared to Figure 3c. Starting with furnace-derived wires (FW), the phase analysis revealed 86.2 wt-% Cr_2GaC and consequently 13.8 wt-% Cr_3C_2 , confirming the successful synthesis suggested by the XRD pattern. Microwave-derived wires (MW) exhibit a similar yield for the MAX phase (82.1 wt-%), however, two more side phases aside from Cr_3C_2 (6 wt-%) are found: Cr_7C_3 (5.8 wt-%) and Cr_2O_3 (5.5 wt-%), as presented in Figure 3a. For full details and results of the refinement, see SI (Tables S 1 - S 6). SEM and EDS studies were carried out to shed light on size, length, and morphology of the obtained wires.

As shown in Figure 2a, the diameter of furnace-derived wires ranges from sub-microns up to about 60 μm , which is the same for microwave-derived wires (see Figure 3a). Hence the method of combustion has no effect on the average diameter, it is fully determined by the spun, pre-combustion wire diameter. The spinning process also results in fused wires of random diameters (see Figure S 3). In the following, we will present the differences between MW and FW in terms of their chemical distribution/microstructure in detail in order to then provide a full discussion on their properties.

The surface morphology of the differently annealed wires differs quite significantly. While FW show a very cratered/scarred outer layer, MW exhibit a smoother, less disrupted, partly even closed surface. This is a counterintuitive observation since the significantly faster reaction times and faster emission of gaseous byproducts during the microwave treatment should lead to a more porous wire surface. In both cases, the surface of the wires is decorated with smaller MAX phase particles in the nm - range (as confirmed by EDS analyses, Figure 2d, and 3d), which makes sense based on the sol-gel based synthesis that involves many small nuclei. Based on EDS quantification, and in contrast to the XRD results, the wires contain a significant amount of carbon (about 96 and 92 at-% for FW and MW, respectively). As this carbon is not visible in XRD, it presents amorphous graphite.

Using AFM, these surface deposited particles were investigated in greater detail. Based on the data shown in Figure 2e, FW depositions have an average height of 131.2 (± 41.8) nm, which is very similar to the average height of MW particles (137.5 ± 46.5 nm, Figure 3e). For the MW, the surface particles are less droplet-like, and in significant numbers, even hexagonally shaped (see Figure 3b, AFM profile Figure 3e) particles. Based on the SEM investigation of the wires, the known side phase Cr_3C_2 must be perfectly mixed into the wire surface, on a very small scale, as high spatial resolution EDS could not identify single Cr_3C_2 particles. However, the MW exhibit a few randomly distributed Ga segregations on the wire surface (see Figure 3d), confirmed by line scans performed across those segregations (Figure S 3). The presence of elemental Ga could have two possible explanations, one being an unreacted, and reduced Ga particle, the other possibility could be rooted in the heating process. Since microwave assisted synthesis have an incredibly fast heating profile,²⁵ Ga could, once reduced, diffuse out of the wire and segregate upon the likewise fast cooling. Similarly, a very recent study by P. Zhang *et al.*²⁶ describes a comparable phenomenon upon pressureless sintering of bulk Cr_2GaC at higher temperatures (1200-1300 $^\circ\text{C}$), a temperature range very easily accomplished in the microwave system.

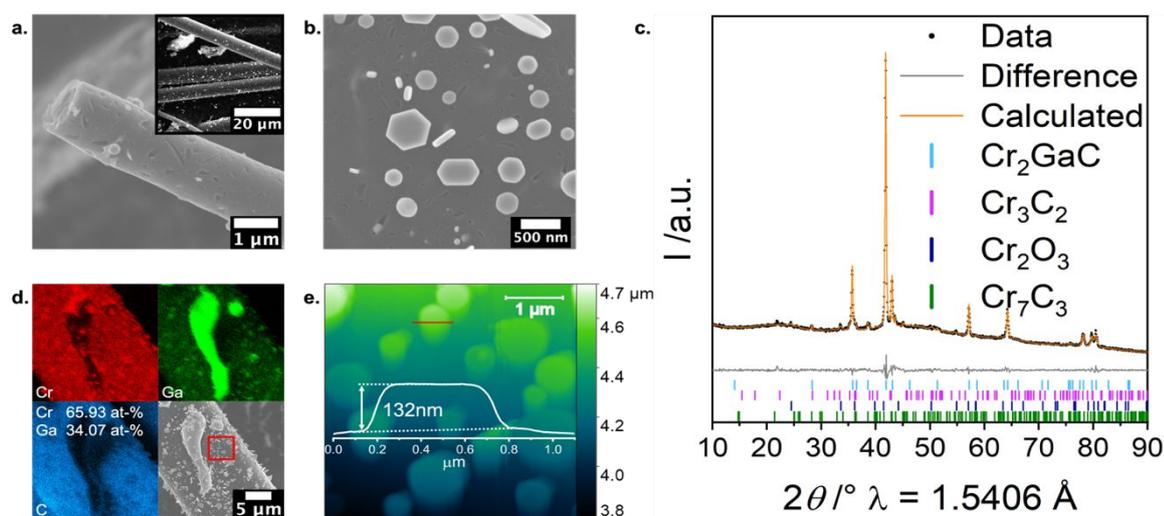


Figure 3: a. SEM micrograph showing a microwave-derived wire. Inset showing multiple micrographs at lower magnification; b. SEM micrograph showing the surface morphology of the microwave-derived microwires, including hexagonally shaped particles; c. Rietveld refinement of microwave-derived Cr_2GaC XRD data, fitted with structural models of Cr_2GaC , Cr_7C_3 , Cr_2O_3 , and Cr_3C_2 ; d. SEM EDS elemental analysis showing the uniform distribution of Cr, Ga, and C around the Ga-segregations sitting on top of the wire surface, as well as the expected 2:1 ratio of Cr:Ga based on the indicated area (red square); e. AFM data (4 x 4 μm) showing the surface depositions as well as an extracted profile (red line, profile overlaid in white), with the shape of the deposition being more rectangular than in Figure 2e.

The inside of the wires also differs depending on the annealing technique. In FW, Cr is prevalent alongside C in the core region (Figure S 1), which indicates Cr_3C_2 accumulation inside the wire, which is in line with the XRD data. The carbon content inside the wires is similar to the amounts measured on the surfaces, however, exact quantifications are difficult to achieve due to the glue used to prepare the cross-sectional view (see SI for more details). Using the Scherrer equation, grain sizes for Cr_3C_2 were determined to be around 650 nm, meaning the Cr_3C_2 phase visible in Figure S 1 represents accumulations of said phase. MW, on the other hand, are entirely homogeneous throughout the entire cross section (Figure S 3, see SI for more details). A potential reason for this difference could stem from the vastly differing heating rates. Particularly the furnace ramping speeds (2 °C per minute) might allow for sufficient crystallite growth and diffusion compared to the drastically faster rates achieved in the microwave oven and result in the differing cross sections. Looking at the different MAX phase grain sizes (also determined by means of XRD), a similar trend is observed: while FW have grain sizes around 190 nm, MW grain sizes amount to only around 70 nm, further supporting the hypothesis of different crystallite growth/mass diffusion rates caused by the different heating techniques.

Electrical properties of Cr_2GaC microwires

As the electronic properties in the mesoscopic range can significantly differ from the bulk counterpart, four-probe resistivity (see Figure 4a) measurements were performed on individual carbonaceous Cr_2GaC microwires. Our goal was to identify the microscopic processes for electron transport in these composite microwires and to understand how the electronic conduction of the microwires differs from conventional MAX phase systems. Previously reported resistivity (ρ) behavior of pelletized Cr_2GaC has been well-described as a traditional metallic temperature dependence.²⁷ The overall resistivity decreases monotonically ($d\rho/dT > 0$) as the temperature decreases²⁷ and is eventually dominated by the defect scattering with signature temperature-independent resistivity at low temperature. Similar responses were also reported for other types of MAX phases and examples include Cr_2GeC ,²⁸ Mn_2GaC ,²⁹ Ti_3AlC_2 ,³⁰ and Ti_3SiC_2 .³¹ On the other hand, graphite, the layered crystalline form of carbon has anisotropic electronic properties due to the presence of van der Waals gap along the crystalline c-axis. While the in-plane conduction is dominated by metallic temperature dependence of resistivity, the out of plane component follows an insulating-like trend with a metal-insulator transition at low temperature.³²

To do a comparative study, we prepared pellets from elemental precursors grown by both microwave and furnace-based methods and performed four-probe resistivity measurement on them. As shown in Figure S 5, bulk samples synthesized both in the microwave oven and furnace follow the conventional metallic trend (see supporting information for synthesis details and characterization, Figure S 4, Tables S 7 and S 8). In contrast to these typical responses from MAX phase pellets, as shown in Figure 4b and 4c, the resistivity of carbonaceous Cr_2GaC microwires increases with decreasing temperature for all furnace-derived samples and for majority of microwave derived samples as opposed to the conventional metallic response. Typical room temperature resistivity values measure in the $\text{m}\Omega\text{m}$ range, which is roughly three orders of magnitude higher compared to the reported metallic Cr_2GaC samples.²⁷ Since the fundamental electronic transport in single crystalline Cr_2GaC is anticipated to be metallic-like (reduced resistivity at low temperature), the observed insulating-like response (increased resistivity at low temperatures) suggests that the electronic transport is dominated by excess amorphous carbon present in the system.

The temperature dependence in Figure 4b and 4c can be well fitted to 3D Mott variable range hopping (VRH) model^{33,34} given by:

$$\rho(T) = \rho_0 \exp\left(\frac{T_{\text{Mott}}}{T}\right)^{0.25} \quad (1)$$

where ρ_0 is a resistivity prefactor and $T_{\text{Mott}} = A/(k_B N(E_f) \xi^3)$ is the characteristic temperature. Here, A is a prefactor taken as 16, k_B is the Boltzman constant, $N(E_f)$ is the density of states at the Fermi level which varies slowly, and ξ is the electron localization length. The fitting of few FW and the MW to this model using the Levenberg Marquardt algorithm is shown in Figure S 6a and S 6b and it suggests a hopping mechanism at a low-T regime (2 K – 170 K). The parameters ρ_0 and T_{Mott} derived from the best fit are listed in Table 1. Using the previously reported $N(E_f)$ value,³⁵ these fitting results have shown that the localization length ξ is in the range of 5.30 - 12.74 nm which agrees well with the amorphous character of carbon. These localization length values signify the decay length of the localized wavefunctions. Small values of ξ compared to the wire dimension is indicative of a necessary hopping mechanism for conduction at low T. We also note that the VRH fitting shows a considerable deviation for some cases at higher temperatures as shown in S 4a which

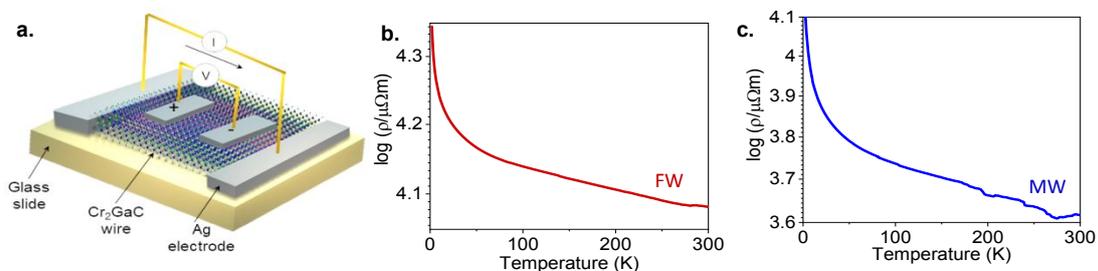


Figure 4: a. Schematic of four-point-probe resistivity(ρ) measurement performed on Cr_2GaC based carbon microwires; b. $\ln(\rho)$ vs. temperature measurement of a typical furnace-grown carbonaceous Cr_2GaC wire c. $\ln(\rho)$ vs. Temperature curve of a typical microwave-grown wire showing insulating trend.

can be related to thermally activated conduction processes^{36,37}.

Table 1: Parameters ρ_0 and T_{Mott} obtained from Mott variable range hopping (VRH) fitting of ρ vs. T data for insulating-like samples.

Synthesis Method	Diameter (μm)	Temperature range (K)	ρ_0 ($\mu\Omega\text{m}$)	T_{Mott} (K)	R^2	Localization Length ξ (nm)
Microwave	73.53 \pm 5.90	2-180	2993.92 \pm 12.53	12.75 \pm 0.26	0.99447	5.30
Furnace	83.16 \pm 1.05	2-150	1174.91 \pm 6.84	1.71 \pm 0.08	0.97509	10.36
Furnace	50.75 \pm 1.40	2-300	604.45 \pm 0.89	0.92 \pm 0.02	0.99449	12.74
Furnace	30.68 \pm 1.39	2-300	417.08 \pm 1.12	1.16 \pm 0.03	0.98823	11.79
Furnace	10.30 \pm 0.47	2-124	99.15 \pm 0.24	1.04 \pm 0.03	0.98110	12.23
Furnace	9.54 \pm 0.20	2-300	201.34 \pm 0.92	1.06 \pm 0.04	0.98745	12.15

While the resistivity of the most of the MW obeys the variable range hopping, we found two other responses from a few MW in their ρ vs. T , namely “metallic” response (Figure S 6c) and a combination of metallic and insulating-like behavior (Figure S 6d). The “metallic” response shown in Figure S 6c can be attributed to crystalline Cr_2GaC as well as graphitization at high temperature during the synthesis and can be modelled as classical Drude metallic resistivity, i.e, $\rho = \rho_0 + \rho_m = \rho_0 + A \cdot T^m$, where ρ_0 is the defect and impurity dominated residual resistivity at low temperatures, A is a temperature dependent weight factor and m is temperature dependent exponent related to different scattering mechanisms. Fitting this expression to the metallic ρ vs. T data at different temperature ranges produces a set of values of ρ_0 , A and m (shown in Table 2) which are reasonable within standard metallic conduction. Analysis of the data at low temperature (11 – 85 K) shows $m \sim 2.3$. Previously, $m \sim 2$ has been reported for metals where the scattering is due to direct electron-electron ($e - e$) interaction,^{38,39} an Umklapp process with large scattered wavevector,⁴⁰ and quantum phase transition (QPT).⁴¹ On the other hand, a T^3 temperature resistivity dependence can be attributed to interband transitions⁴² of conduction electrons. Hence, we attribute the $T^{2,3}$ dependence to the interplay of $e - e$ scattering, Umklapp process, and interband scattering of the conduction electrons. The high temperature regime (210 – 300 K) of the metallic curve gives rise to T -linear dependence which originates from increased electron-phonon interaction at elevated temperature. The scattering phenomena at the intermediate range (85 – 210 K) are most probably a combination of the low and high-temperature interactions as mentioned above.

The last observed response in MW is non-monotonic behavior, as shown in Figure S 6d, best described as a transition or cross-over between insulating and metallic-like behavior. One potential reason for such a unique response might be associated with disorder induced multiple scattering in the electronic states near Fermi level (E_f), such as quantum interferences due to weak localization^{43,44} and electron-electron interaction in a disordered system.^{45,46} Here, another possibility is the series resistivity contribution from insulating-like response (from amorphous carbon) with lower room temperature resistance and metallic-like conduction (from Cr_2GaC) with high r_0 value. In such a case, as the temperature is lowered, the total resistivity is dominated by the insulating response once the metallic resistivity drops below the insulating range. We note that a similar non-monotonic response has been observed in graphite, graphite-

based compounds, and carbon nanotubes and the electrical response still remains open to questions and our studies warrant future studies in the field.⁴⁷

Halide treatment process

Chemical doping is a powerful strategy to improve electrical conductivity. Previously, halide-based doping has been used to engineer the electrical conductivity of carbonaceous materials including graphite,⁴⁸ graphene,⁴⁹ polymers,⁵⁰ and carbon nanotubes.⁵¹ We have employed a halide treatment in a MAX phase based system for the first time to boost their electrical properties. Here, the porous surface and low-dimensionality of carbonaceous MAX phase Cr_2GaC microwires offer large surface to volume ratios and promote greater degrees of interaction with the halides (bromine or iodine vapor). Besides the surface architecture, vdW gaps in amorphous carbon provides ample scope for halogen intercalation between carbon layers.

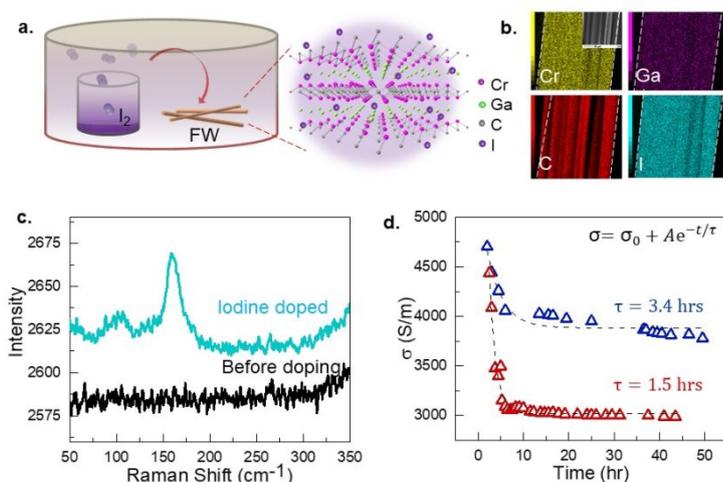


Figure 5: a. schematic of iodine treatment in FW b. EDS mapping of Cr, Ga, C and I after iodine treatment in carbonaceous Cr_2GaC microwires; c. Raman spectra before and after iodine treatment; iodine anion peaks are located around 101 cm^{-1} and 160 cm^{-1} ; d. Time dependent conductivity of iodinated microwires showing improved conductivity through iodine treatment.

Considering the chemical incompatibility of Au or Ag electrical contacts with the halide vapors, we first subjected the FW microwires to iodine (or bromine) vapor at 200° C for 1.5 and 2.0 hours (red and blue symbols in Figure 5c, respectively) and created 4-terminal contacts after the treatment to access their transport properties. Figure 5a represents a schematic of iodine treatment of Cr₂GaC wires. After the iodine treatment, the presence of iodine in Cr₂GaC MAX phase based wires was confirmed by EDS elemental mappings (Figure 5b, and S 7). Our estimates from EDS semi-quantitative analysis (Figure S 7) performed within 2 hours of exposure shows uniform distribution of iodine. The presence of iodine can be further evidenced by the prominent iodine anion Raman peaks located at 101 and 160 cm⁻¹ (Figure 5c), corresponding to the stretching modes of I₃⁻ and I₅⁻ anions formed by charge transfer within the carbonaceous Cr₂GaC wire.⁵² No Raman peak corresponding to molecular iodine (180 cm⁻¹) eliminates the possibility of iodine accumulation inside the material.

Measurement of time dependent electronic properties after halogen treatment can give insights into the diffusion dynamics of the volatile dopants, which can be useful for gas sensing applications. After the iodine exposure (for bromine, see Figure S 8), the time-

Table 2: Parameters σ_0 , A and τ derived from $\sigma = \sigma_0 + Ae^{-t/\tau}$ fitting to the ρ vs. t data of iodinated Cr₂GaC.

Wire radius (μm)	Treatment time (hr)	σ_0 (S/m)	A (S/m)	τ (hr)
35.55 \pm 1.68	1.5	3017.90 \pm 12.67	7986.20 \pm 1101.90	1.4 \pm 0.1
21.51 \pm 0.67	2	3884.01 \pm 23.03	1399.22 \pm 269.77	3.4 \pm 0.8

dependent conductivity (Figure 5d) of the iodinated individual microwires was measured again. Here the time axis refers to the time after the halogen treatment is completed. The overall conductivity increases significantly after halogen treatment and falls with time t following the equation in the form of $\sigma = \sigma_0 + Ae^{-t/\tau}$, see fitted curves in dashed lines in Figure 5d. This clearly indicates that the conductivity of the wires can be improved by a simple post-processing halogen treatment technique. Here, the parameter σ_0 is the saturation conductivity. A is the difference between conductivity at time $t = 0$ and σ_0 , and τ correspond to the characteristic time for decay. From A and σ_0 values derived from the fitted

data, it was found that the conductivity was enhanced by 260 % and 36 % for two wires shown in Figure 5d, suggesting halogen diffusion is highly effective in boosting the electrical properties. The parameters obtained from fitting are listed in Table 3. In our experiment, τ changes within the order of hours (Figure 5d). Since iodine is present inside the wires in anion form, the treatment is likely to increase the conductivity by increasing the overall hole carrier density. As the conductivity shows a time response mainly described by the diffusion process, it also suggests that iodine anions diffuse out of the MAX phase matrix with time coefficients of 1.5 and 3.4 hours. Similar time dependent conductivity data is shown in Figure S 8d. Though the gas sensing properties of ceramic MAX phase samples are not well explored, this time dependent conductivity response of doped samples makes carbonaceous Cr₂GaC microwires potential candidates for chemiresistive halogen gas sensors.⁵³

Conclusion. We report on the first-ever successful synthesis of carbonaceous Cr₂GaC MAX phase microwires, a shape only achievable via a modified sol-gel approach. Utilizing conventional furnace heating as well as non-conventional microwave heating, we are able to obtain vastly differing microstructures, especially in terms of surface structure and homogeneity. While furnace-derived microwires exhibit Cr-rich cores and cratered surfaces, microwave-derived microwires appear to be homogenous throughout with smoother and closed surfaces. Leveraging advanced low temperature electronic transport measurements, we discovered transport behavior of the microwires, which ranges from metallic- to insulating-like, as well as combinations thereof. Building on this fundamental understanding, we introduced halides (I and Br) into the layered structure of the microwires in order to engineer their electronic properties. Time-resolved measurements revealed a conductivity boost of more than 200 %, as well as showed a time-dependent decrease of the boosted conductivity. Based on these findings, we propose MAX phase Cr₂GaC based microwires as (potential) candidates for chemiresistive halogen gas sensors.

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Keywords: sol-gel processes, solid-state reactions, MAX phase, Cr₂GaC, microwire, four-point probe resistivity measurement

References

1. Barsoum, M. W. The $M_{N+1}AX_N$ phases: A new class of solids. *Prog. Solid State Chem.* **28**, 201–281 (2000).
2. Radovic, M. & Barsoum, M. W. MAX phases: bridging the gap between metals and ceramics. *Am. Ceram. Soc. Bull.* **92**, 20–27 (2013).
3. Maniv, A. *et al.* Microscopic evidence for Mn-induced long range magnetic ordering in MAX phase compounds. *J. Phys. Condens. Matter* **33**, 025803 (2021).
4. Rivin, O. *et al.* Evidence for ferromagnetic ordering in the MAX phase $(Cr_{0.96}Mn_{0.04})_2GeC$. *Mater. Res. Lett.* **5**, 465–471 (2017).
5. Rohde, H. & Kudielka, H. Strukturuntersuchungen an Carbosulfiden von Titan und Zirkon. *Zeitschrift für Krist. - Cryst. Mater.* **114**, 447–456 (1960).
6. Jeitschko, W., Nowotny, H. & Benesovsky, F. Kohlenstoffhaltige ternäre Verbindungen (H-Phase). *Monatshefte für Chemie* **94**, 672–676 (1963).
7. Jeitschko, W., Nowotny, H. & Benesovsky, F. Kohlenstoffhaltige ternäre Verbindungen (V-Ge-C, Nb-Ga-C, Ta-Ga-C, Ta-Ge-C, Cr-Ga-C und Cr-Ge-C). *Monatshefte für Chemie* **94**, 844–850 (1963).
8. Etzkorn, J., Ade, M., Kotzot, D., Kleczek, M. & Hillebrecht, H. Ti_2GaC , Ti_4GaC_3 and Cr_2GaC - Synthesis, crystal growth and structure analysis of Ga-containing MAX-phases $M_{n+1}GaC_n$ with $M=Ti, Cr$ and $n=1, 3$. *J. Solid State Chem.* **182**, 995–1002 (2009).
9. Han, Y. *et al.* Design of Hetero-Nanostructures on MoS_2 Nanosheets to Boost NO_2 Roomtemperature Sensing. *ACS Appl. Mater. Interfaces* **10**, 22640–22649 (2018).
10. Arya, N., Avasthi, P. & Balakrishnan, V. A light-fostered supercapacitor performance of multi-layered ReS_2 grown on conducting substrates. *Nanoscale Adv.* **3**, 2089–2102 (2021).
11. Wu, Y. H., Yu, T. & Shen, Z. X. Two-dimensional carbon nanostructures: Fundamental properties, synthesis, characterization, and potential applications. *J. Appl. Phys.* **108**, (2010).
12. Hong, S. *et al.* Highly sensitive active pixel image sensor array driven by large-area bilayer MoS_2 transistor circuitry. *Nat. Commun.* **12**, 1–11 (2021).
13. Balderston, S. *et al.* Discrimination of single-point mutations in unamplified genomic DNA via Cas9 immobilized on a graphene field-effect transistor. *Nat. Biomed. Eng.* **5**, 713–725 (2021).
14. Xu, H., Shang, H., Wang, C. & Du, Y. Ultrafine Pt-Based Nanowires for Advanced Catalysis. *Adv. Funct. Mater.* **30**, 1–18 (2020).
15. Law, M. *et al.* Nanoribbon waveguides for subwavelength photonics integration. *Science (80-)*. **305**, 1269–1273 (2004).
16. Zhao, Y. S. *et al.* Optical waveguide based on crystalline organic microtubes and microrods. *Angew. Chemie - Int. Ed.* **47**, 7301–7305 (2008).
17. Lee, S. H. *et al.* Room-Temperature, Highly Durable $Ti_3C_2T_x$ MXene/Graphene Hybrid Fibers for NH_3 Gas Sensing. *ACS Appl. Mater. Interfaces* **12**, 10434–10442 (2020).

18. Offermans, P., Crego-Calama, M. & Brongersma, S. H. Functionalized vertical InAs nanowire arrays for gas sensing. *Sensors Actuators, B Chem.* **161**, 1144–1149 (2012).
19. Jiang, M., Mao, W., Zhou, X., Kan, C. & Shi, D. Wavelength-Tunable Waveguide Emissions from Electrically Driven Single ZnO/ZnO:Ga Superlattice Microwires. *ACS Appl. Mater. Interfaces* **11**, 11800–11811 (2019).
20. Chen, S. *et al.* Ionic liquid-assisted synthesis of N/S-double doped graphene microwires for oxygen evolution and Zn–air batteries. *Energy Storage Mater.* **1**, 17–24 (2015).
21. Chai, G. Y. *et al.* Fabrication and characterization of an individual ZnO microwire-based UV photodetector. *Solid State Sci.* **13**, 1205–1210 (2011).
22. Hamm, C. M., Schäfer, T., Zhang, H. & Birkel, C. S. Non-conventional Synthesis of the 413 MAX Phase V_4AlC_3 . *Zeitschrift für Anorg. und Allg. Chemie* **642**, 1397–1401 (2016).
23. Hamm, C. M., Bocarsly, J. D., Seward, G., Kramm, U. I. & Birkel, C. S. Non-conventional synthesis and magnetic properties of MAX phases $(Cr/Mn)_2AlC$ and $(Cr/Fe)_2AlC$. *J. Mater. Chem. C* **5**, 5700–5708 (2017).
24. Coelho, A. A. TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++. *J. Appl. Crystallogr.* **51**, 210–218 (2018).
25. Siebert, J. P., Hamm, C. M. & Birkel, C. S. Microwave heating and spark plasma sintering as non-conventional synthesis methods to access thermoelectric and magnetic materials. *Appl. Phys. Rev.* **6**, 041314 (2019).
26. Zhang, P. *et al.* Mechanism and mitigation of spontaneous Ga whisker growth on Cr_2GaC . *Sci. China Technol. Sci.* **63**, 440–445 (2019).
27. Lin, S. *et al.* Magnetic and electrical/thermal transport properties of Mn-doped $M_{n+1}AX_n$ phase compounds $Cr_{2-x}Mn_xGaC$ ($0 \leq x \leq 1$). *J. Appl. Phys.* **113**, 053502 (2013).
28. Lin, S. *et al.* Alloying effects on structural, magnetic, and electrical/thermal transport properties in MAX-phase Cr_2-xM_xGeC ($M = Ti, V, Mn, Fe, \text{ and } Mo$). *J. Alloys Compd.* **680**, 452–461 (2016).
29. Novoselova, I. P. *et al.* Large uniaxial magnetostriction with sign inversion at the first order phase transition in the nanolaminated Mn_2GaC MAX phase. *Sci. Rep.* **8**, 1–11 (2018).
30. Goc, K. *et al.* Structure, morphology and electrical transport properties of the Ti_3AlC_2 materials. *Ceram. Int.* **44**, 18322–18328 (2018).
31. Barsoum, M. W. *et al.* Electrical conductivity, thermopower, and Hall effect of Ti_3AlC_2 , Ti_4AlN_3 , and Ti_3SiC_2 . *Phys. Rev. B* **62**, 10194–10198 (2000).
32. Tongay, S. *et al.* Supermetallic conductivity in bromine-intercalated graphite. *Phys. Rev. B - Condens. Matter Mater. Phys.* **81**, 1–6 (2010).
33. Mott, Nevill Francis, and E. A. D. Electronic processes in non-crystalline materials. *Oxford Univ. Press* (2012).
34. Yanming Sun *et al.* Electrical conductivity of single polycrystalline-amorphous carbon nanocoils. *Carbon N. Y.* **98**, 285–290 (2016).
35. Tong, H. *et al.* Difference in physical properties of MAX-phase compounds Cr_2GaC and Cr_2GaN induced by an anomalous structure change in Cr_2GaN . *Intermetallics* **105**, 39–43 (2019).

36. Halim, J. *et al.* Variable range hopping and thermally activated transport in molybdenum-based MXenes. *Phys. Rev. B* **98**, 1–11 (2018).
37. Zubair Ansari, M. & Khare, N. Thermally activated band conduction and variable range hopping conduction in $\text{Cu}_2\text{ZnSnS}_4$ thin films. *J. Appl. Phys.* **117**, (2015).
38. Poker, D. B. & Klabunde, C. E. Temperature dependence of electrical resistivity of vanadium, platinum, and copper. *Phys. Rev. B* **26**, 7012–7014 (1982).
39. Lin, X., Fauque, B. & Behnia, K. Scalable T² resistivity in a small single-component Fermi surface. *Science (80-.)*. **349**, 945–948 (2015).
40. Wallbank, J. R. *et al.* Excess resistivity in graphene superlattices caused by umklapp electron–electron scattering. *Nat. Phys.* **15**, 32–36 (2019).
41. J. A. N. Bruin, 1 H. Sakai, 1 R. S. Perry, 2 A. P. Mackenzie. Similarity of Scattering Rates in Metals Showing T-Linear Resistivity. *Science (80-.)*.
42. Webb, G. W. Low-temperature electrical resistivity of pure niobium. *Phys. Rev.* **181**, 1127–1135 (1969).
43. Bergmann, G. Weak localization in thin films. *Phys. Scr.* **1986**, 99 (1986).
44. Thompson, R. S., Li, D., Witte, C. M. & Lu, J. G. Weak Localization and Electron–Electron Interactions in Indium-Doped ZnO Nanowires. *Nano Lett.* **9**, 3991–3995 (2009).
45. Dutta, P., Mandal, S. K., Dey, P., Lakhani, A. & Yusuf, S. M. A comparative study in different rare earth ions in multiferroic nanocomposites: Low temperature resistivity minima and low field magnetoresistance. *J. Magn. Magn. Mater.* **502**, (2020).
46. Lee, P. A. & Ramakrishnan, T. V. Disordered electronic systems. *Rev. Mod. Phys.* **57**, 287–337 (1985).
47. Fischer, J. *et al.* Metallic resistivity in crystalline ropes of single-wall carbon nanotubes. *Phys. Rev. B - Condens. Matter Mater. Phys.* **55**, R4921–R4924 (1997).
48. Li, J., Vaisman, L., Marom, G. & Kim, J. K. Br treated graphite nanoplatelets for improved electrical conductivity of polymer composites. *Carbon N. Y.* **45**, 744–750 (2007).
49. Majee, S., Banerjee, D., Liu, X., Zhang, S. L. & Zhang, Z. B. Efficient and thermally stable iodine doping of printed graphene nano-platelets. *Carbon N. Y.* **117**, 240–245 (2017).
50. Hsu, S. L., Signorelli, A. J., Pez, G. P. & Baughman, R. H. Highly conducting iodine derivatives of polyacetylene: Raman, XPS, and x-ray diffraction studies. *J. Chem. Phys.* **69**, 106–111 (1978).
51. Fan, L. & Xu, X. A stable iodine-doped multi-walled carbon nanotube-polyppyrrrole composite with improved electrical property. *Compos. Sci. Technol.* **118**, 264–268 (2015).
52. Jung, N., Crowther, A. C., Kim, N., Kim, P. & Brus, L. Raman enhancement on graphene: Adsorbed and intercalated molecular species. *ACS Nano* **4**, 7005–7013 (2010).
53. Kim, S. J. *et al.* Metallic $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Gas Sensors with Ultrahigh Signal-to-Noise Ratio. *ACS Nano* **12**, 986–993 (2018).