

## Supporting Information

### Towards a mechanistic understanding of the sol-gel syntheses of ternary carbides

Jan P. Siebert<sup>a</sup>, Mikkel Juelsholt<sup>b</sup>, Damian Günzig<sup>c</sup>, Heiko Wende<sup>c</sup>, Katharina Ollefs<sup>c</sup>, Christina S. Birkel<sup>\*a,d</sup>

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#### Synthesis

A typical synthesis was based off 100 mg Cr<sub>2</sub>GaC. The precursors Cr- and Ga-nitrate (Sigma Aldrich and Alfa Aesar, respectively), and citric acid (Alfa Aesar) were used without further purification, and weighed in air. Based on the MAX phase stoichiometry, 2 equivalents of the Cr- and 1 equivalent of the Ga precursor alongside a ninefold citric acid excess (9 equivalents), which translates to 0.4314 g Cr-nitrate (1.078 mmol), 0.159 g Ga-nitrate (0.539 mmol), and 0.932 g citric acid (4.851 mmol). The precursors were dissolved in ~10 mL deionized water, and upon complete dissolution the mixture was heated to about 80 °C until a viscous gel was obtained. Without further processing, the gel was transferred into an alumina combustion boat, and placed into a tube furnace (Carbolite, model EST), which allows for a controlled atmosphere. After flushing the tube for 30 minutes with Ar, the gel was heated with 2 °C per minute to 1050 °C. This temperature was held for 5 hours before allowing the furnace to cool to room temperature

naturally. During the entire combustion process an Ar atmosphere (~0.2 L per minute) was upheld. The obtained porous, black product was ground into a fine powder for characterization.

## Rietveld Refinement XRD Data

Rietveld refinements were carried out in Topas<sup>1</sup>, using crystal structures from ICSD<sup>2</sup>. Generally, a sample displacement factor, scale factor, background, lattice parameters, profile, thermal displacement factors (Beq), occupancies, and phase compositions were refined. Typically, the refinement process started with establishing the background and displacement factor prior to fitting a crystal structure. The background polynomial was initially set to an order of 10. Next, the lattice parameters of the phase were alternately refined with the profile, whereas for the latter a modified Thompson-Cox-Hastings pseudo-Voigt function (pV-TCHZ) was used with the parameters  $u$ ,  $v$ ,  $w$ , and  $x$ . After obtaining the best possible fit with this procedure, atom positions were refined (in case of Cr<sub>2</sub>GaC only the  $z$  value of the Cr site), as well as thermal displacement factors and occupancies.

Below, in Tables S 1 - S 4, the refined parameters of each refined phase are listed. The phase fractions are given in wt-% behind each phase.  $R_{\text{Bragg}}$  is given for each individual phase, whereas the  $R_{\text{wp}}$  is given for each complete refinement, including all fitted phases.

### Cr<sub>2</sub>GaC 1050 °C

Table S 1: Refined parameters of Cr<sub>2</sub>GaC, based on XRD data (1050 °C). Errors in parentheses.

Cr <sub>2</sub> GaC (83.7(2) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.0845(2)	0.964(9)	0.7(2)
Ga1	0.3333	0.6667	0.75	0.949(2)	0.0(2)
C1	0.00	0.00	0.00	1	0
a /Å			2.89129(3)		
c /Å			12.6090(2)		
a <sup>3</sup> /Å <sup>3</sup>			2.88		
c <sup>3</sup> /Å <sup>3</sup>			12.61		
R <sub>Bragg</sub>			2.873		
R <sub>wp</sub>			3.61		

Table S 2 Refined parameters of Cr<sub>3</sub>C<sub>2</sub>, based on XRD data of Cr<sub>2</sub>GaC (1050 °C). Errors in parentheses.

Cr <sub>3</sub> C <sub>2</sub> (16.2(2) wt%)	x	y	z	Occupancy	Beq
Cr1	0.0132(9)	0.2500	0.4012(4)	0.93(2)	0
Cr2	0.1732(8)	0.2500	0.7741(4)	0.93(2)	0
Cr3	0.8660(9)	0.2500	0.9312(5)	1	0.505
C1	0.070(5)	0.2500	0.205(3)	1	0.82
C2	0.236(4)	0.2500	0.957(3)	1	0.83
a /Å			5.52414(8)		
b /Å			2.82883(4)		
c /Å			11.4905(2)		

$a^4 / \text{\AA}$	5.5329(5)
$b^4 / \text{\AA}$	2.8290(2)
$c^4 / \text{\AA}$	11.4719(7)
$R_{\text{Bragg}}$	0.780
$R_{\text{wp}}$	3.61

### $\text{Cr}_2\text{GaC}$ 800 °C

Table S 3: Refined parameters of  $\text{Cr}_2\text{GaC}$ , based on XRD data (800 °C). Errors in parentheses.

<b><math>\text{Cr}_2\text{GaC}</math> (25.4(2) wt%)</b>	<b>x</b>	<b>y</b>	<b>z</b>	<b>Occupancy</b>	<b>Beq</b>
Cr1	0.3333	0.6667	0.0821(4)	0.952(7)	0.7(2)
Ga1	0.3333	0.6667	0.75	1	0.0(2)
C1	0.00	0.00	0.00	1	0)
$a / \text{\AA}$			2.89565(5)		
$c / \text{\AA}$			12.6047(3)		
$a^3 / \text{\AA}$			2.88		
$c^3 / \text{\AA}$			12.61		
$R_{\text{Bragg}}$			0.517		
$R_{\text{wp}}$			2.79		

Table S 4: Refined parameters of  $\text{Cr}_2\text{O}_3$ , based on XRD data of  $(\text{Cr}_{1-x}\text{Mo}_x)_2\text{GaC}$  (800 °C). Errors in parentheses.

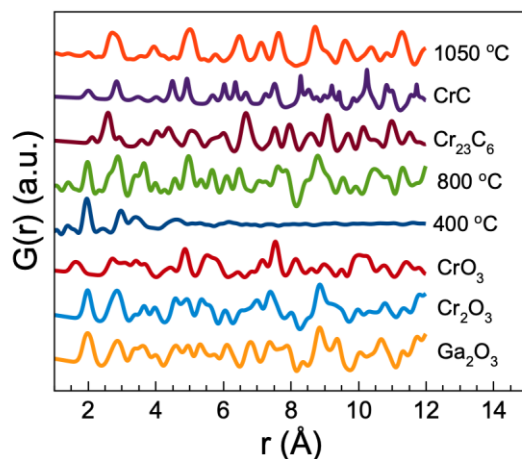
<b><math>\text{Cr}_2\text{O}_3</math> (74.4(2) wt%)</b>	<b>x</b>	<b>y</b>	<b>z</b>	<b>Occupancy</b>	<b>Beq</b>
Cr1	0.0000	0.0000	0.34773(7)	0.925(2)	0.06(3)
O1	0.3089(5)	0.0000	0.2500	0.988(3)	0.78(6)
$a / \text{\AA}$			4.96322(8)		
$c / \text{\AA}$			13.5856(3)		
$a^5 / \text{\AA}$			4.960(2)		
$c^5 / \text{\AA}$			13.599(5)		
$R_{\text{Bragg}}$			1.055		
$R_{\text{wp}}$			2.79		

## Scanning Electron Microscopy

SEM analysis was performed on a Zeiss Auriga FIB, equipped with a SDD EDS detector from Oxford instruments (Ultim MAX). All samples were mounted on an aluminum stub via adhesive carbon tape, and analyzed without any further preparation. The microscope was operated at acceleration voltages ranging between 5 and 20 keV.

## Total Scattering and Pair Distribution Function Analysis

The total scattering data was obtained at Deutsches Elektronen Synchrotron (DESY) at beamline P02.1 and Oakridge National Laboratory's Spallation Neutron Source using the Nanoscale-Ordered Materials Diffractometer (NOMAD). The PDFs were obtained as described in the main text and modelled using PDFgui25. In all refinements a scale factor, the unit cell parameters, the atomic positions and isotropic atomic displacement parameters were refined. The correlated motion between atoms was described using the  $\delta_2$ -parameter and the effect of the crystallite size was described using a spherical dampening, the SPdiameter in PDFgui. The atomic positions and the unit cell parameters were refined in the reported space group symmetry, except for the disordered graphite model used in the fit in Figure 8c. Here the space group symmetry was broken to allow the C atoms to move along the crystallographic *c*-axis of the hexagonal unit cell. In the fits shown in Figures 6 in the main, as well as Figure S5 the occupancies of the tetrahedral sites were also refined. In the fit in Figure 6b the tetrahedral occupancy was linked to the occupancy of the neighboring octahedral site as described in the main text. The refined parameters are shown in table S12-S17.



**Figure S 1:** Comparison between the X-ray PDFs obtained from the samples synthesized at 1050 °C and 400 °C, along with the calculated X-ray PDFs from different gallium and chromium oxides, as well as chromium carbides.

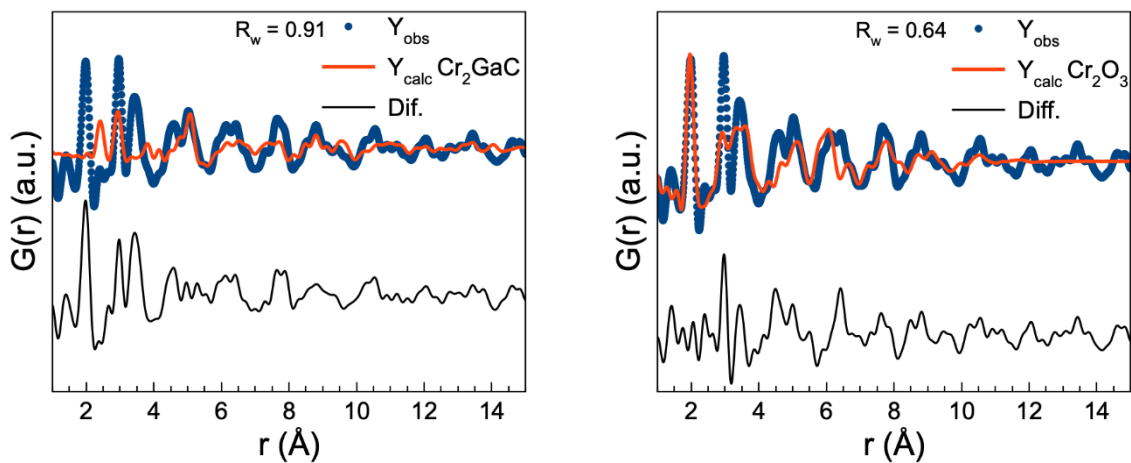


Figure S 2: Fit of  $\text{Cr}_2\text{GaC}$  (left) and  $\text{Cr}_2\text{O}_3$  (right) to the PDF obtained from the 725 °C sample.

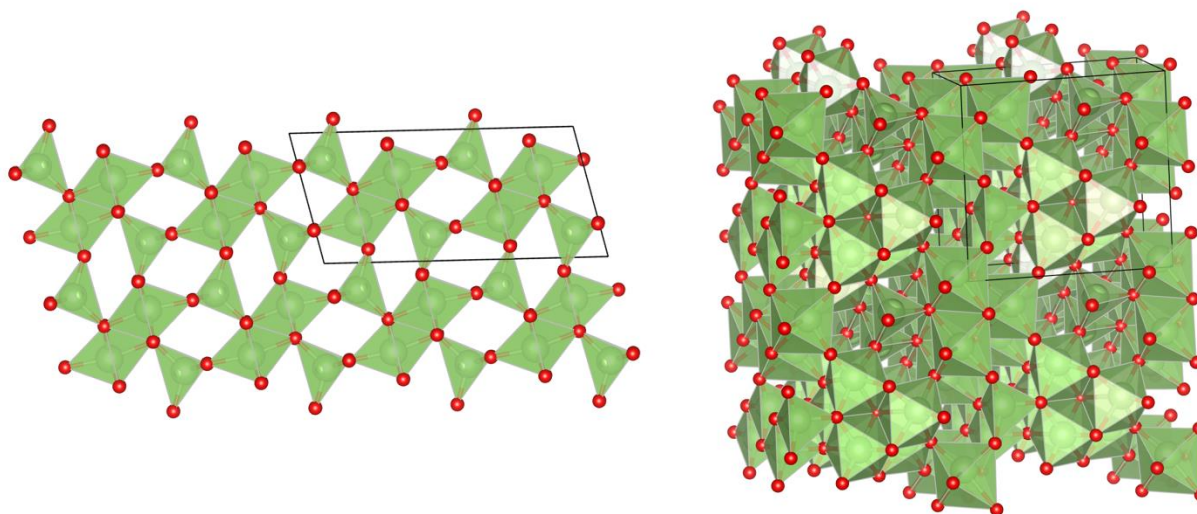
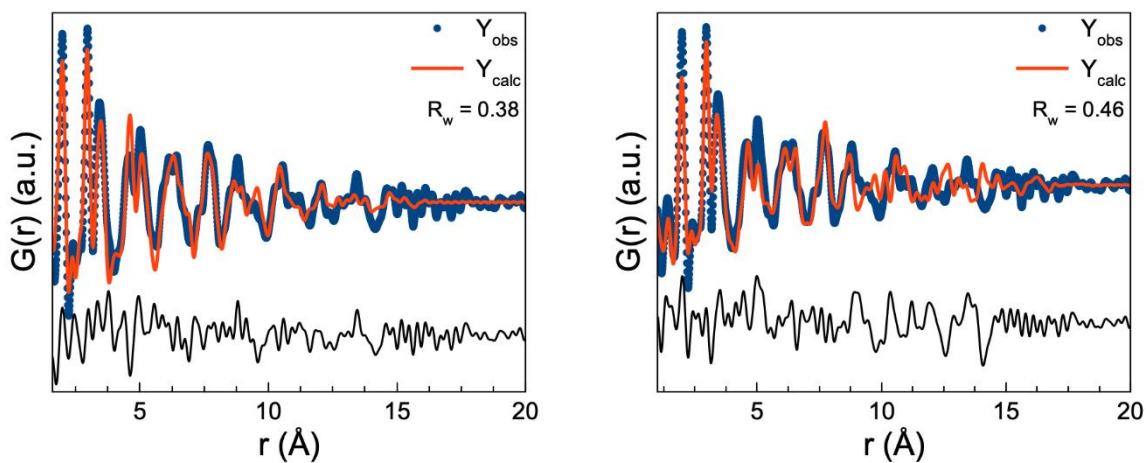


Figure S 3: Fit of  $\beta\text{-Ga}_2\text{O}_3$ <sup>6</sup> (left) and  $\epsilon\text{-Ga}_2\text{O}_3$ <sup>7</sup> (right) to the PDF obtained from the 725 °C sample. Below each fit is the structure of the two phases with Ga shown in green and O in red.

Table S 5: Refined parameters for the fit in Figure 6a.

	Space group	Fd-3mZ			
a	$\delta_2$	SPdiameter	$R_w$		
8.25 Å	3.49 Å <sup>2</sup>	16.55 Å	0.45		
	x	y	z	Uiso (Å <sup>2</sup> )	occ
Ga	0.125	0.125	0.125	0.018	0.42
Ga	0.5	0.5	0.5	0.010	1
O	0.257	0.257	0.257	0.018	1

Table S 6: Refined parameters for the fit in Figure 6b.

	Space group	I41/amd			
a	c	$\delta_2$	SPdiameter	$R_w$	
11.52 Å	8.62 Å	3.44 Å <sup>2</sup>	17.14 Å	0.38	
	x	y	z	Uiso (Å <sup>2</sup> )	occ
Ga	0.611	0.0	0.0	0.006	0.72
Ga	0.0	0.107	0.223	0.006	1
Ga	0.0	0.75	0.125	0.006	1
Ga	0.25	0.5	0.875	0.006	0.28
Ga	0.129	0.0	0.0	0.006	1
O	0.131	0.006	0.277	0.003	1
O	0.0	0.097	-0.006	0.003	1
O	0.0	0.143	0.514	0.003	1

Table S 7: Refined parameters for Cr<sub>2</sub>GaC in the fit in Figure 7c.

	Space group	P6 <sub>3</sub> /mmc			
a	c	$\delta_2$	$R_w$		
2.89 Å	12.59 Å	3.21 Å <sup>2</sup>	0.22		
	x	y	z	Uiso (Å <sup>2</sup> )	occ
Cr	0.333	0.666	0.25	0.007	1
Ga	0.666	0.333	0.086	0.004	1
C	0.0	0.0	0.0	0.004	1

Table S 8: Refined parameters for the graphite phase in the fit in Figure 7c.

Space group		P1			
a	b	c	$\alpha$	$\beta$	$\gamma$
2.45 Å	2.45 Å	7.65 Å	90	90	120
$\delta_2$	SPdiameter	$R_w$			
1.05 Å <sup>2</sup>	11.4 Å	0.22			
	x	y	z	Uiso (Å <sup>2</sup> )	occ
C	0.0	0.0	0.22	0.002	1
C	0.0	0.0	0.76	0.002	1
C	0.3333	0.6666	0.19	0.002	1
C	0.6666	0.3333	0.74	0.002	1

Table S 9: Refined parameters for Cr<sub>3</sub>C<sub>2</sub> in the fit in Figure 7c.

Space group		Pnma			
a	b	c	$\delta_2$	$R_w$	
5.53 Å	2.84 Å	11.38 Å	3.26 Å <sup>2</sup>	0.22	
	x	y	z	Uiso (Å <sup>2</sup> )	occ
Cr	0.010	0.25	0.414	0.001	1
Cr	0.232	0.25	0.775	0.001	1
Cr	0.876	0.25	0.930	0.001	1
C	0.133	0.25	0.204	0.004	1
C	0.206	0.25	0.955	0.004	1

## X-ray Absorption Spectroscopy

### EXAFS Fitting Parameters

The parameters fitted to the measurements described in the main part, can be found in Table S10 for the Cr K-edge. Here, N describes the path degeneracy,  $R_{fit}$  the fitted distance to the neighbor atom,  $\sigma^2$  the mean squared displacement,  $S_0^{2*}$  the amplitude reduction factor, which was determined by Cr foil, and  $\Delta E$  the energy difference between simulation and experiment. For the 900°C sample, the whole structure was fitted. Instead of an  $R_{fit}$  an isotropic factor  $\alpha_{fit}$  of -0.02(39) % was used to describe the mismatch between experiment and simulation in lattice parameters for the Cr K-edge. At the Ga K-edge, an  $\alpha_{fit}$  of 0.77(19) % can be found, the other fitted parameters can be found in Table S 11.

Table S 10: Fitting parameters from EXAFS measurements and simulations for Cr K-edge measurements.

	path	N	$R_{fit}$ [Å]	$\sigma^2$ [Å <sup>2</sup> ]	$S_0^{2*}$	$\Delta E$ [eV]
300°C	Cr – O	6*	1.9677(77)	0.00184(63)	0.63	-7.13(0.94)
600°C	Cr – C	3*	2.015(20)	0.00200(163)	0.63	-9.44(2.87)

	Cr – Cr	3*	2.931(20)	0.00541(35)	0.63	-9.44(2.87)
<b>900°C</b>	Cr <sub>2</sub> GaC	-	-	0.01066(97)	0.63	4.46(1.42)

Table S 11: Fitting parameters from EXAFS measurements and simulations for Ga K-edge measurements.

	path	N	R <sub>fit</sub> [Å]	σ <sup>2</sup> [Å <sup>2</sup> ]	S <sub>0</sub> <sup>2*</sup>	ΔE [eV]
<b>300°C</b>	Ga – O	6*	1.954(11)	0.00675(84)	0.90	-2.52(1.30)
<b>600°C</b>	Ga – O	4.68(27)	1.869(7)	0.00476(92)	0.90	-1.74(1.00)
<b>900°C</b>	Cr <sub>2</sub> GaC	-	-	0.00500(37)	0.90	2.39(1.02)

## Near-Edge Spectroscopy

The EXAFS measurements also carry information about the valence state of the absorbing atom, if the near-edge is recorded with sufficient resolution. The presented near-edge spectra are extracted from the EXAFS measurement, which are described in the main part. For the Cr K-edge, near-edge calculations were performed using the software FEFF.<sup>8,9</sup> At the Cr K-edge near-edge spectra we found a good agreement between simulation and experiment, showing the transition from Cr<sub>2</sub>O<sub>3</sub> to Cr<sub>2</sub>GaC.

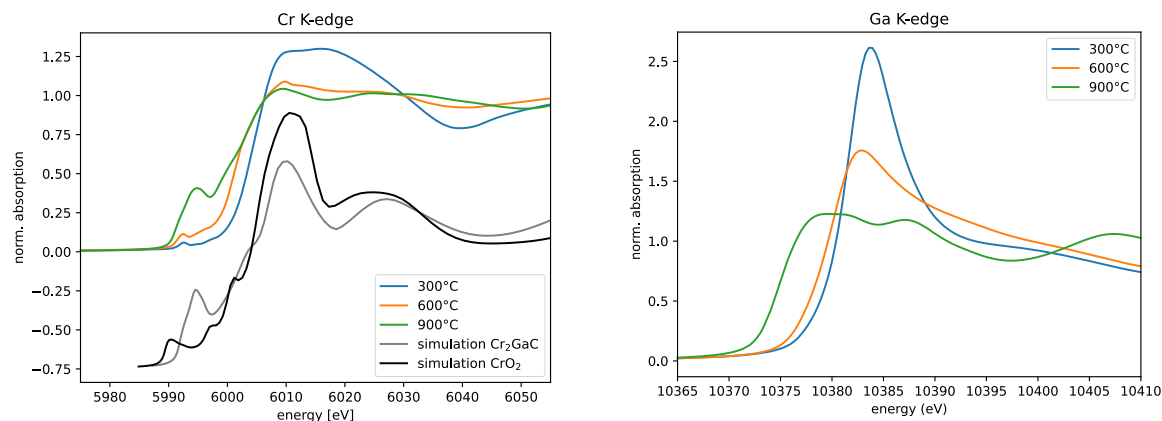


Figure S 4: (a) Cr K-edge XANES measurements and near edge simulations carried out by FEFF (b) Ga K-edge XANES measurements. All shown spectra are part of the whole EXAFS measurements described in the main part.

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