Supplementary Information for

Sol-gel based synthesis and enhanced processability of MAX phase Cr_2GaC

Jan Paul Siebert, Lothar Bischoff, Maren Lepple, Alexander Zintler, Leopoldo Molina-Luna, Ulf Wiedwald and Christina S. Birkel

Synthesis

For a typical synthesis, the nitrate precursors $Cr(NO_3)_3*9H_20$ (Honeywell, 98%) and $Ga(NO_3)_3*xH_2O$ (ChemPUR, 99,9%, please note, the amount of H_2O was determined to be 8 formula units by TGA measurements) and citric acid (Alfa Aesar, 99,5%) were weighed in air and dissolved in a minimal amount of DI-water (usually 10 ml). We typically used a ratio of 2:1 for Cr:Ga ($Cr(NO_3)_3*9H_20$: 2.695 mmol = 1.0784 g, $Ga(NO_3)_3*8H_2O$: 1.3475 mmol = 0.5398 g) and a threefold molar excess of citric acid (0.012 mol = 2.33 g) based on the amount of all metals. After mixing the precursor compounds with water using a magnetic stir bar inside a beaker, the homogenous solution was heated to 70 °C – 80 °C on a heating plate until a viscous liquid was obtained. The gel was then transferred into a Al_2O_3 crucible in which the heat treatment was conducted. During the annealing process, the temperature was increased with a rate of 2 °C/min up to 900 °C using a tube furnace (Carbolite). The final temperature was held for five hours bevor cooling down to room temperature. The heat treatment took place under argon to prevent the formation of oxygen impurities.

A second sample was prepared with an even larger excess of citric acid: In that case, we used a Cr:Ga:citric acid ratio of 2:1:20, for example in 0.539 mmol (0.2159 g) Ga, 1.078mmol (0.4314 g) Cr and 10.78 mmol (2.0711 g) citric acid.

Characterization

X-ray powder diffraction (XRD)

For the X-ray diffraction measurement, the product was crushed using an agate mortar and pistil and the obtained powder was then loaded into a polyimide (Kapton) capillary. High resolution synchrotron powder diffraction data were collected at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using X-rays with wavelength λ = 0.412624 Å. For the laboratory X-ray diffraction measurements, the powder sample was loaded onto a flat plat holder and measured with a powder diffractometer system STOE STADI P with monochromatized Cu radiation in transmission geometry. Rietveld refinements were obtained using the program TOPAS (Topas Academic v4.1, Alan Coelho, Brisbane, Australia).

Simultaneous Thermal Analysis (STA)

Thermal analysis combined with on-line mass spectroscopic analysis was executed on a Netzsch STA 449 F3 Jupiter® and QMS 403 C Aelos in flowing Ar (50 ml/min). For the analysis, approximately 85 mg of the freshly prepared and fully dried gel (~15 h at 100 °C) was measured in corundum crucibles from room temperature to 1050 °C with a heating rate of 10 °C/min. The heat effects of the reactions were detected using differential thermal analysis (DTA), the mass changes were monitored using thermal gravimetry (TG) and the pyrolysis and reaction products were analyzed simultaneously using mass spectrometry (MS).

High-resolution scanning electron microscopy (HREM)

Morphology and particle size were characterized using a high-resolution scanning electron microscope (Philips XL30 FEG, 20-30 kV acceleration voltage) equipped with an Energy Dispersive X-ray Spectrometer (EDS, EDAX Genesis). Conductive carbon tabs mounted on aluminum specimen holders were used for adhering the samples prepared from ground products.

Transmission electron microscopy (TEM)

TEM samples were fabricated out of the ground/powdered sample by ultrasonically dispersing the powder (20 mg) in ethanol (10 mL) for 15 hours. The dispersion was drop cast on a holey carbon grid. (S)TEM (Fig. 6) was performed on a JEOL ARM-200F operated at 200 kV. Diffraction patterns were recorded on a Gatan US1000. Imaging conditions for HAADF-STEM have been selected as probe size 6C, a condenser aperture of 30 µm and a camera length of 6 cm. Energy dispersive X-ray spectroscopy was performed on a JEOL JEM-2100F operated at 200 kV. Acquisition settings were selected with a condenser aperture of 50 µm and a camera length of "HAADF5" or 7.6 cm. EDS spectra have been recorded on an Oxford X-Max 80 mm² detector.

HAADF-STEM image simulation

For HAADF-STEM image simulation along the [010] zone axis QSTEM[1] was used. According to the experimental conditions, a C_S value of 1 µm, a C_C value of 1 mm and an energy spread of 1.0 eV were assumed. HAADF detection angles were set to 90-360 mrad.

Magnetometry

The magnetic properties were determined by vibrating sample magnetometry (VSM) in a Quantum Design PPMS DynaCool system. The sample powder (m = 11.30 mg) was manually pressed in a capsule. The magnetization and magnetic susceptibility have been determined by field- and temperature-dependent scans.

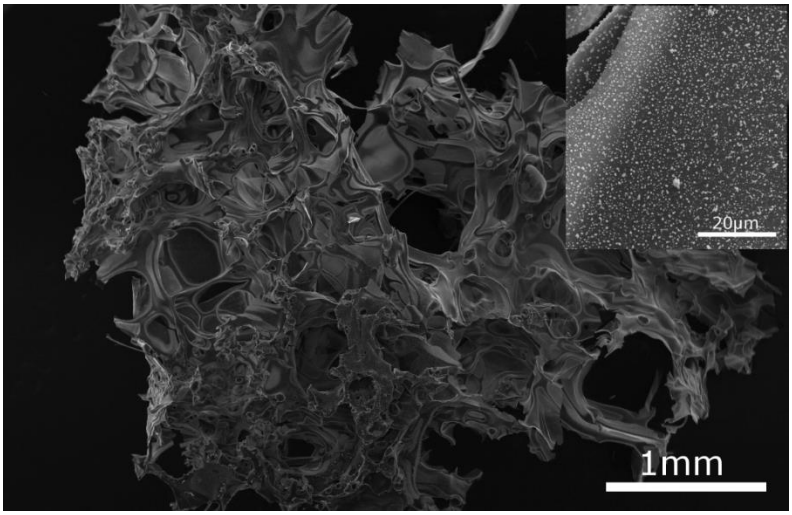

Fig. SI-1 Scanning electron micrograph of the product obtained after annealing (not ground) showing its porous character. The light particles on its surface visible at a higher magnification (inset) are most likely amorphous carbon.

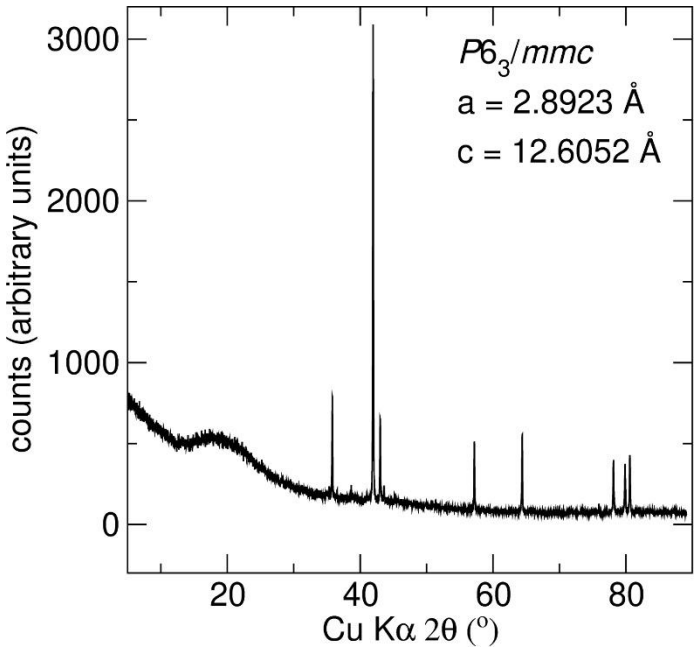

Fig. SI-2 X-ray powder diffraction data of MAX phase Cr_2GaC prepared by the sol-gel method with a higher excess of citric acid. The additional peak at around 43° most likely corresponds to very small amounts of Cr_3Ga.

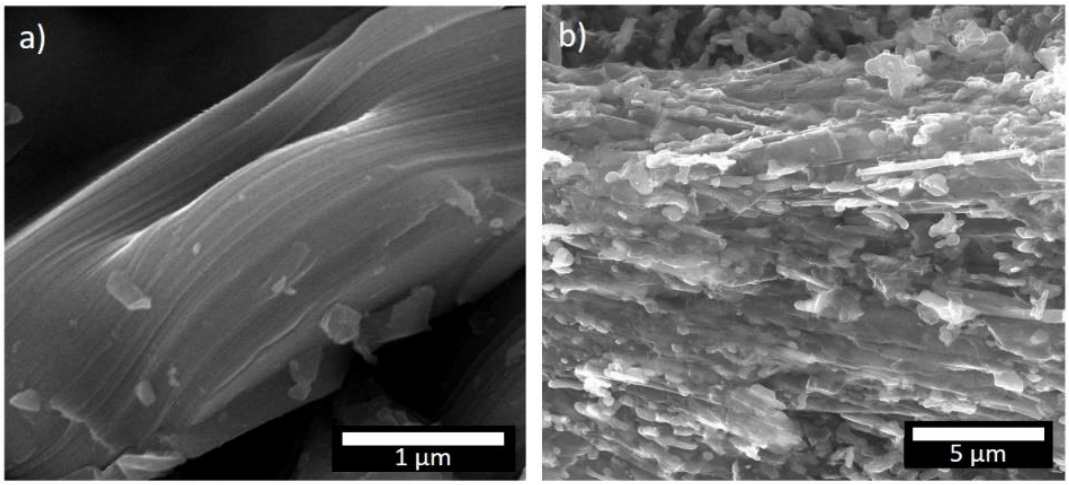

Fig. SI-3: HRSEM micrographs of Cr_2GaC showing differences in morphology resulting from solid-state synthesis (a) and sol-gel synthesis (b).

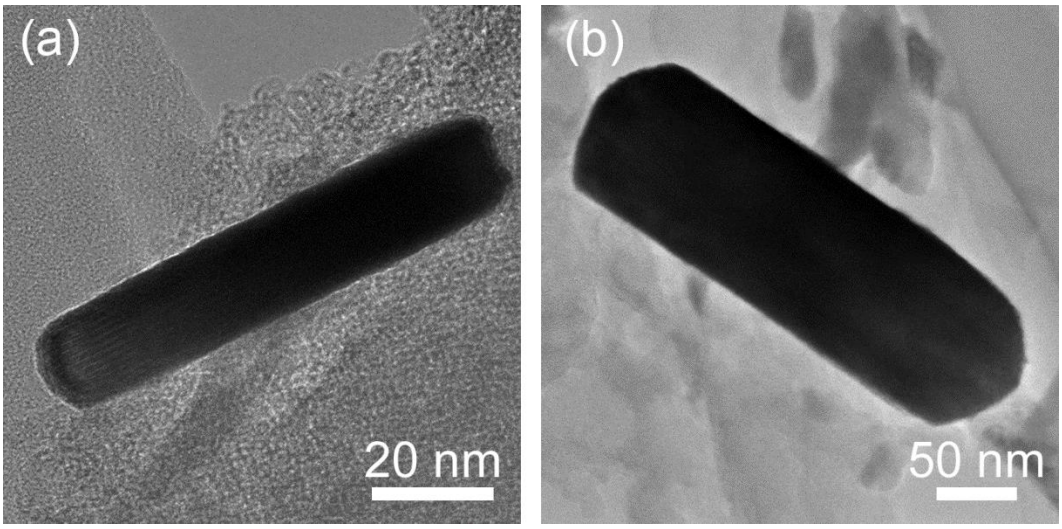

Fig. SI-4 Transmission electron micrographs of the product showing different needle-like particles as well as amorphous areas.

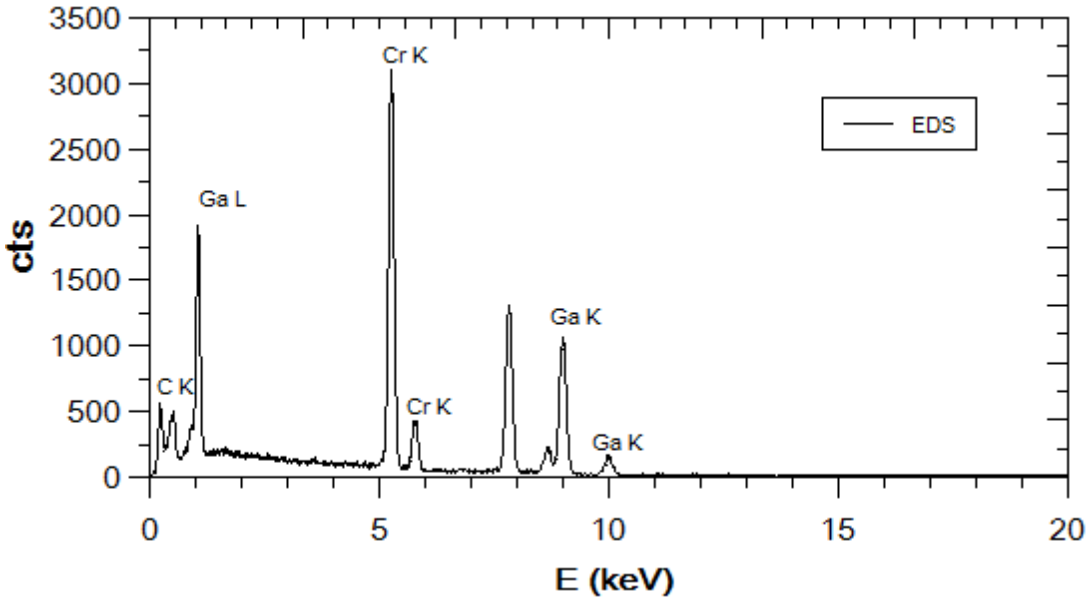

Fig. SI-5 EDS spectrum of an analyzed particle. Additional peaks are stray Cu radiation from the copper grid.

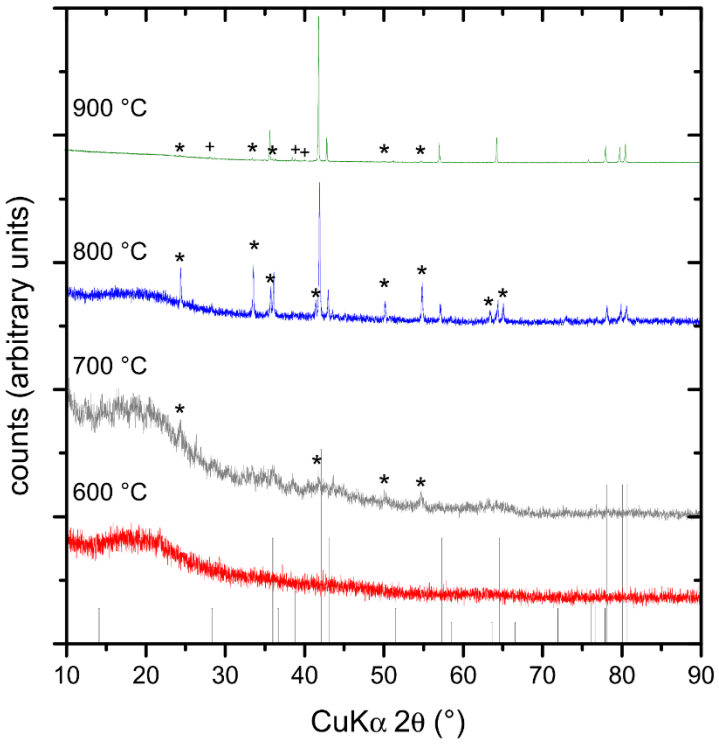

Fig. SI-6 X-ray powder diffraction data of the product after annealing the precursor gel at 600 °C (red), 700 °C (grey), 800 °C (blue) and 900 °C (green), respectively showing the transformation of an amorphous into a crystalline compound while reducing the amount of oxides (Cr_2O_3 indicated with stars, Cr_3C_2 indicated with crosses (side phase in final product)).

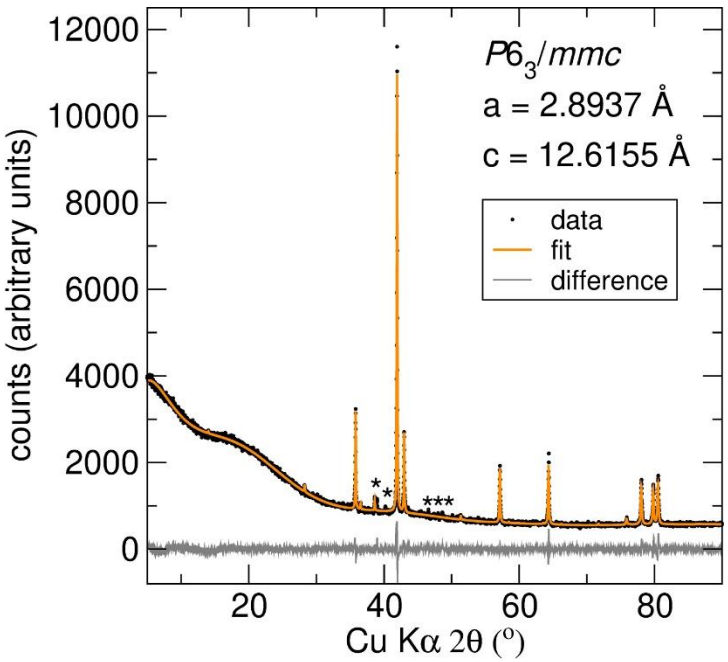

Fig. SI-7 X-ray powder diffraction data of MAX phase particles decorated on amorphous hollow carbon spheres prepared. Stars indicate the presence of a minor amount of Cr_3C_2 as a side phase.

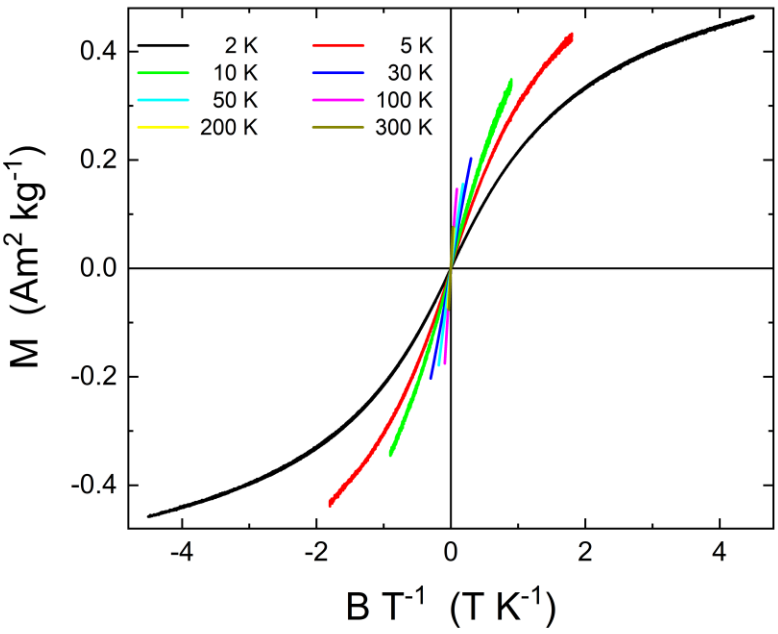

Fig. SI-8 Magnetization as function of the ratio of induction *B* and temperature *T*.