Experimental Report

Experiment number: *CH-6474*

Experimental title: *Synthesis and single-crystal X-ray diffraction characterization of novel yttrium carbides under high pressure up to 200 GPa*

Despite the richness of organic chemistry, the main structural motifs of the "carbon" framework in compounds are limited and repeated. Most of the recently known metal carbides contain the simplest carbon anions: isolated carbon atoms C^{4-}, $[C_2]^{2-}$ and linear $[C_3]^{4-}$ units, which have the same carbon skeleton as methane, acetylene, and allene. High pressure (HP) alters the bonding patterns in carbides, leading to new compounds with unusual structural units and interesting properties, and as such, compression might enable exploring the catenation of carbon. The Rare-Earth (RE) carbide family shows a large variety of phases even at ambient pressure with different stoichiometry (e.g., for RE = Y: Y_2C, Y_4C_5, Y_3C_4, Y_2C_3, Y_4C_7, YC_2). A small number of experimental HP studies on the Y-C system, the availability of theoretical predictions of exotic RE carbides structures, as well as the possibility of discovering new superconducting phases make it relevant to study the RE-C system at HP.

Experiment

XRD measurements were performed at the ID27 beamline of the ESRF with the X-ray beam (λ = 0.3738 Å) focused down to 1.5 × 1.5 μm^2, XRD patterns were collected on an Eiger2X CdTe 9 M hybrid photon-counting pixel detector. For single-crystal XRD measurements, samples were rotated in a range ±36°. The XRD images were collected with an angular step $\Delta\omega$ = 0.5° and an exposure time of 2s per frame. Five wide-opening (± 36°) BX90 diamond anvil cells (DAC) with a small piece of RE (RE = Y, Nd, Sm, and Gd) in paraffin oil were compressed at home laboratory. Laser-heating was performed using in house laser heating setup , equipped with two YAG lasers (1064 nm central wavelength).

Results

The chemical reaction of yttrium and paraffin oil at pressures of ~50 GPa and temperatures of ~2500°C led to the synthesis of a previously unknown polymorph of yttrium carbide, orthorhombic γ-Y_4C_5. Reaction products were characterized by synchrotron SCXRD. The carbon atoms in the γ-Y_4C_5 crystal structure form $[C_2]$ dumbbells and nonlinear $[C_3]$ trimers with the bending angle of 134.4(1)° (Fig.1). Usually, $[C_3]$ units in known carbides are linear or almost linear with bending angle 170-180° and which is in consistence with organic analog—allene, therefore bending angle of 134.4(1)° in γ-Y_4C_5 is indeed unique. Density functional theory-based calculations demonstrate the metallic nature of γ-Y_4C_5 and its dynamic stability at the synthesis pressures. They also indicate that above 12 GPa γ-Y_4C_5 is thermodynamically favorable relative to α-Y_4C_5. Charge distribution analysis revealed non-integer charges of carbon units, $[C_2]^{5.24-}$ and $[C_3]^{6.76-}$. This specific charge distribution results in unusual C-C bond orders of 1.38 and 1.31, respectively, and a considerable previously never observed bending of the $[C_3]$ units. Since rare-earth (RE) metals and their known carbides usually behave similarly at HP-HT conditions, it is important to examine if other RE metals also form the γ-RE_4C_5. We tested this on Nd, Sm, and Gd metals that we laser-heated to ~3000 K in paraffin oil at 70 GPa and 85 GPa, leading to the synthesis of the carbides with the same structural motifs.

Thus, carbon polymerization under high pressure can drastically change the common arrangement of carbon atoms in metal carbides and their physical properties.

Conclusions

The aim of the experiment has been partially achieved, the RE-C (RE = Y, Nd, Sm, and Gd) system must be further studied at higher pressures in order to expand the field of new exotic polycarbon entities in metal carbides.

The publication is under preparation and the ID27 stuff will be included as a co-author.