Experiment Report Form

	Experiment title: Synthesis of Rare-Earth Carbides at High-Pressure in Laser-Heated DACs	**Experiment number**: HC-5184
Beamline: ID11	**Date of experiment**: from: 20.06.2023 to: 23.06.2023	**Date of report**: 08.09.2023
Shifts: 9	**Local contact(s)**: Wright Jonathan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Akbar Fariia Iasmin[1]*, Dubrovinsky Leonid[1], Laniel Dominique[2], Liang Akun[2]*, Ranieri Umbertoluca[2*], Aslandukov Andrii[1,3*], Aslandukova Alena[1]

[1] Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI), University of Bayreuth, Universitaetsstrasse 30, 95440 Bayreuth, Germany

[2] Centre for Science at Extreme Conditions and School of Physics and Astronomy, University of Edinburgh, Edinburgh EH93FD, United Kingdom

[3]Material Physics and Technology at Extreme Conditions, Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany

Report:

Carbides represent a diverse group of compounds important in science and technology due to their intriguing chemical, mechanical, electrical, magnetic and optical properties. Structural variations observed in carbides, driven by composition and external factors such as pressure and temperature, often lead to the formation of compounds with distinct types of chemical bonding and captivating crystal chemistry. The synthesis and investigation of rare-earth metal carbides under high pressure allows to produce new types of compounds and find the relationship between their structures and properties. The aim of the proposed experiment at ESRF ID11, was to apply methods of single-crystal X-ray diffraction (XRD) in laser-heated diamond anvil cells (DACs) in order to determine crystal structures and chemical compositions of possible high-pressure phases in Ln-C systems.

Metallic La, Gd, Dy and Yb were placed on one anvil and surrounded with NaCl used as a pressure medium in DACs. The samples were laser-heated at 42-95 GPa to 2800(200) K. For pressure determination at beamline the EOS of NaCl-B2 was used. Direct reaction of lanthanides with carbon from diamond anvils resulted in the synthesis of at least two novel lanthanides carbides phases consisting of naphthalene fragments (Fig. 1): 1) LaC_2 synthesized at 45 and 67 GPa (sp. gr. *C2/m*; $Z = 10$, $a = 7.889(15)$ Å, $b = 5.829(2)$ Å, $c = 6.9647(19)$ Å, $\beta = 95.39(6)°$ at 45 GPa) and 2) La_3C_5 (sp. gr. *C2/m*; $Z = 4$, $a = 4.869(12)$ Å, $b = 10.846(5)$ Å, $c = 7.366(4)$ Å, $\beta = 107.79(13)°$ at 45 GPa). Moreover, previously discovered at 41 GPa LaC-type structure comprising carbon dumbbells was reproduced for LaC at 45 GPa (sp. gr. *Cmcm*; $Z = 8$, $a = 3.2725(5)$ Å, $b = 12.0688(14)$ Å, $c = 5.360(3)$ Å); the novel Dy_4C_3[1] phase was synthesized in Dy-C system at higher pressure – 95 GPa with unit cell parameters: sp. gr. *I*-43*d*; $Z = 4$; $a = 6.6798(8)$ Å. This structural type containing discrete carbon atoms was found as a product of high-pressure high-temperature synthesis in Gd-C and Yb-C systems: Gd_4C_3 (sp. gr. *I*-43*d*; $Z = 4$; $a = 7.187(2)$ Å at 46 GPa) and Yb_4C_3 (sp. gr. *I*-43*d*; $Z = 4$; $a = 7.0138(11)$ Å at 42 GPa). Recently discovered γ-Y_4C_5-type structure[2] consisting of carbon [C_2] and [C_3] units was found to be reproducible for Gd_4C_5 (sp. gr. *Cmce*; $Z = 8$, $a = 12.451(6)$ Å, $b = 7.585(2)$ Å, $c = 8.7969(13)$ Å at 45 GPa), Dy_4C_5 (sp. gr. *Cmce*; $Z = 8$, $a = 11.8201(18)$ Å, $b = 7.275(7)$ Å, $c = 8.3476(13)$ Å at 65 GPa) and Yb_4C_5 (sp. gr. *Cmce*; $Z = 8$, $a = 12.0074(6)$ Å, $b = 7.4694(11)$ Å, $c = 8.6251(8)$ Å at 42 GPa).

Discovered structures (Fig. 1) demonstrated an existence of carbon arrangements previously unobserved at ambient conditions. The reproduction of novel structures for a number of lanthanides confirms the presence of regularities in the chemistry of lanthanides under high pressures. Therefore, high-pressure high-temperature synthesis allows to significantly extend the range of known lanthanides carbides and gives an opportunity to discern trends in the chemistry of lanthanides under extreme conditions.

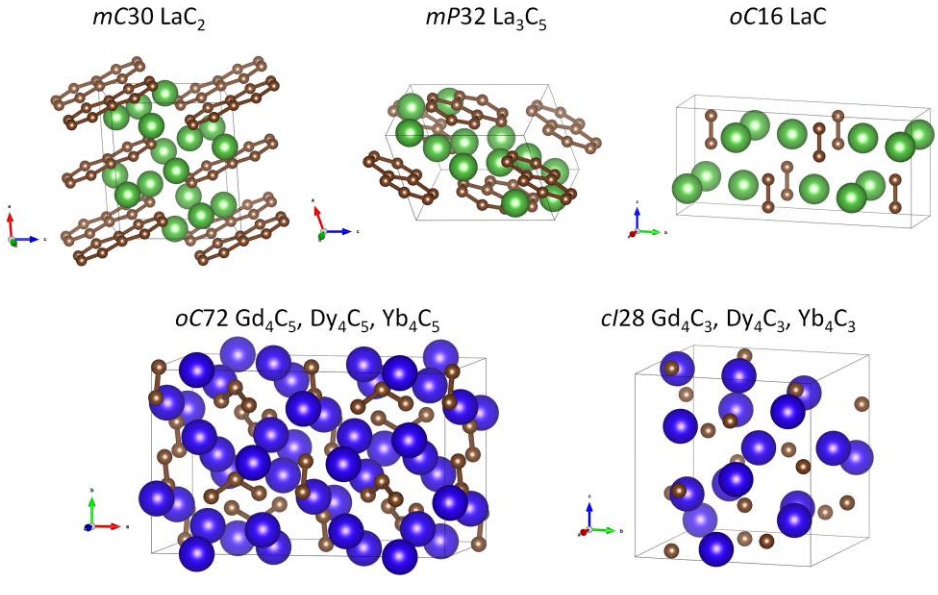

Figure 1. Crystal structure of novel high-pressure phases of lanthanides carbides: *mC*30 LaC, *mP*32 La_3C_5, *oC*16 LaC (obtained earlier at lower pressure), Gd_4C_5 (reproduced for Dy and Yb) and Dy_4C_5 (reproduced for Gd and Yb).

1. Akbar, F. I. *et al.* High-pressure synthesis of dysprosium carbides. *Front. Chem.* **11**, 1–9 (2023).

2. Aslandukova, A. *et al.* Novel High-Pressure Yttrium Carbide γ-Y4C5 Containing [C2] and Nonlinear [C3] Units with Unusually Large Formal Charges. *Phys. Rev. Lett.* **127**, 135501 (2021).