Tracing peculiar diamond nanostructures

NKFI KH-17 126502 Final Report

The goal of this research was the complex study of diamond nanocrystals building on the previous breakthrough results of the project leader. We aimed to investigate unusual diamond nanostructures in natural and synthetic samples, elucidate their structural details and properties as well as provide insights into the mechanism that is responsible for their occurrence. In accordance with the call of the KH-17 proposal we targeted to obtain outstanding scientific achievements in an international context.

The project was successful from all aspects and its outcome was not influenced by change of the team members. Our state-the-art multi-analytical characterization on a range of synthetic and natural diamonds revealed fundamentally new information on their unique structure and properties. In particular, we reported the existence of a new class of carbon materials (referred as diaphites) that combines the superhard qualities of diamond with improved fracture resistance and increased plasticity as well as pointed out the wide variety of fascinating and complex nanostructures contained within meteorites, impacted rocks, and laboratory-shocked samples that can be targeted to produce future diamond-related materials with improved mechanical, thermal and optoelectronic properties.

The most significant results have been published in the leading material science journals such as **Nature Materials**, **ACS Nano Letters** and **Scientific Reports**, and they were reported in **American Mineralogist** and are in review in **Ceramics International**. One paper about the fundamentally new interpretation of nanodiamond structures is in its near final version and is planned to be submitted to the highest prestige **Nature** journal in January 2021. The cumulative impact factor for the published papers is **61.757**. In order to point out the significance of the findings and to raise the public awareness of the topic, press materials were published at the ELKH and TTK websites. The participants of the projects reported their results at national and international conferences and seminars.

Major results

1. Diamond-Graphene composite nanostructures

During the structural analysis of natural impact and laboratory-shocked graphite and diamonds, we discovered a new class of carbon materials that combine the super-hardness of diamond with the excellent flexibility of graphene. According to our paper (1) published in ACS Nano Letters, the new materials, which occur in impact diamond and laboratory-shocked graphite samples, are not simply mechanical mixtures of diamond and graphene, but true structural intergrowths at the nanoscale having well-defined bonding interfaces between the two types of carbon regions. We referred these diamond-graphene nanocomposites as “diaphites” to illustrate the intimately bonded diamond and graphitic units that make up the structure.

We demonstrated, through a multi-methodological approach, that diamond-graphene nanostructures exist within extended 3D materials and that they form two related but distinct structural families depending on the angle of the bonds formed between the graphitic and diamond domains. We found that diaphites exist with relatively low energy competitive with graphite and diamond, i.e., they are readily achievable and are expected to be kinetically stable. Diaphites are therefore candidates for obtaining recoverable metastable carbon materials formed during static or dynamic compression and can be encountered during the compression phase or the rarefaction wave associated with impact shock or during their recovery to ambient conditions. Thus their occurrence could also aid toward understanding the formation conditions and history of meteorites. The diaphite nanocomposites represent a new class of high-performance carbon materials that preserve the superhard and incompressible properties of the diamond units, while leading to fracture toughening due to the angular flexibility and tensile resistance of the graphitic domains bonded to them.

The new results were published in **ACS Nano Letters** and a Hungarian (http://www.ttk.hu/aktualis-hirek/plasztikus-gyemantok) and an English (http://www.ttk.hu/en/recent-news/ductile-diamonds) news material were posted on the TTK website. The project leader was the first and a corresponding author of the paper.

2. *Complex nanostructures in diamond*

In this contribution (2) we highlighted and classified the structural complexity of diamonds found in meteorites and laboratory-shocked samples by applying a systematic hierarchical approach and investigated their energetic stability. In particular, we described the intriguing complexity of cubic-hexagonal stacking disorder and nanotwinned structures, layered graphene domains included within covalently-bonded carbon, diamond units contained within graphitic materials as well as rounded fullerene-type nanostructures and twinned structures with unusual five-fold rotational symmetries. We pointed out that so far these complex nanostructures have been identified mainly among meteorite samples or impacted rocks, or shown to be present in laboratory-shocked materials. Some structures were prevalent among millimetre-sized samples, others constituted only a small fraction of the overall volume, but according to theoretical calculations they existed at relatively low energy and were expected to be kinetically stable. They are therefore candidates for obtaining larger scale metastable carbon materials formed by static or dynamic compression that are recoverable to ambient conditions.

We suggested the nanostructures can be targeted for preparing materials with exceptional hardness as well as improved fracture toughness and ductility. Furthermore, they can be attractive for engineering the electronic conductivity as well as the optical and thermoelectric properties of diamond. We concluded that engineering the next generations of complex carbon nanostructures for new applications is just entering its infancy.

The new results were published in **Nature Materials** and a Hungarian and an English news material were posted on both on the ELKH (https://elkh.org/en/news/a-member-of-the-research-centre-for-natural-sciences-is-the-leader-of-an-international-project-aimed-at-researching-complex-nanostructures-for-engineering-next-generation-diamond-related-materials/) and the TTK (http://www.ttk.hu/en/recent-news/complex-nanostructures-for-engineering-next-generation-diamond-related-materials) websites. The project leader was the first author of the paper.

3. *Nanodiamonds exhibiting six- and twelve-fold symmetries*

Our ultra-high resolution TEM (uHRTEM) images of individual 3-5 nm nanodiamonds (NDs) revealed an abundance of unusual six-fold as well as crystallographically forbidden twelve-fold symmetries (3) that are not permitted among sp3-bonded structures even considering twinning arrangements available for both cubic- and hexagonally-stacked diamond layers. Combining our uHRTEM observations with density functional theory (DFT) calculations we demonstrated how these nanostructures arose as a result of intimately-bonded graphene-diamond (diaphite) domains containing sp2- and sp3-bonded assemblages. The interpretations are supported by X-ray diffraction, Raman and electron energy-loss spectroscopy for our and previously studied samples combined with first principles modeling. We proposed that diaphites, containing 2-3 layer thick graphene layers compressed by the interfacial bonding to diamond, occur throughout synthetic and natural nanodiamonds. Observation of these unexpected architectures within natural and synthetic NDs confirms the suggestion that the family of sp2-/sp3-bonded diaphites could constitute a new class of carbons spanning the range between diamond and graphitic to few-layered graphene, that can be produced under readily accessible laboratory conditions and that persist as metastable forms of the element over geological timescales at ambient conditions. Their existence helps us understand and control the remarkable mechanical and tribological properties observed for NDs and recognition of the few-layered graphene nanostructures coherently bonded to and embedded within the diamond matrix leads to prediction and control of further nanomechanical and optoelectronic properties. The metallic graphene nanostructures embedded within the wide-gap semiconducting diamond host formed by laser waveguide channeling can be used as potential charge storage devices with external contacts, whereas selective incorporation of N and other defects within the unique structures and their interfaces can provide controlled insertion of magnetically or electronically active centers.

The new results were incorporated into a manuscript (3), which is in its near final form and planned to be submitted to the highest prestige **Nature** journal in January 2021 with the PI being the first and corresponding author. A pre-submission inquire was sent to Karl Ziemelis, the chief physical sciences editor of Nature, who encouraged the submission of our ms as soon as possible.

4. *Extraterrestrial, shock-formed, cage-like nanostructured carbonaceous materials*

We discovered carbon nano-onions and bucky-diamonds in a shock-formed meteorite (Gujba). The nano-onions were fullerene-type materials and ranged from 5 to 20 nm; the majority showed a graphitic core-shell structure, and some were characterized by fully curved, onion-like graphitic shells. The core was either filled with carbonaceous material or empty. We identified the first, natural, 4-nm-sized bucky-diamond, which is a type of carbon nano-onion consisting of multilayer graphitic shells surrounding a diamond core. We proposed that the nano-onions formed during shock metamorphism of the pre-existing primitive carbonaceous material that included nanodiamonds, poorly-ordered graphitic material, and amorphous nanospheres. Bucky-diamonds could have formed either through the high-pressure transformation of nano-onions, or as an intermediate material in the high-temperature transformation of nanodiamond to nano-onion. We pointed out that shock-formed nano-onions and bucky-diamonds are fullerene-type structures, and as such could be relevant for explaining the astronomical 217.5 nm absorption feature.

The new results were published in **American Mineralogist** (4). The project leader was the first and the corresponding author of the paper.

5. *Quantifying hexagonal stacking in diamond*

We investigated natural impact and laboratory-shocked diamonds and found their structure could be characterized by the so-called hexagonality number, which provides a measure for hexagonal layer stacking in cubic diamonds. Using the MCDIFFaX approach for analyzing X-ray diffraction data, hexagonality indices up to 40% were identified. The effects of increasing amounts of hexagonal stacking on the Raman spectra of diamond were investigated computationally and found to be in excellent agreement with trends in the experimental spectra. Transmission electron microscopy revealed nanoscale twinning within the cubic diamond structure. Our analyses lead us to propose a systematic protocol for assigning specific hexagonality attributes to the mineral designated as lonsdaleite among natural and synthetic samples.

We published the new results in the **Scientific Reports** journal (5). The project leader was one of the corresponding authors of the paper.

6. *High-temperature evolution of diamond –SiC composites*

The excellent material properties found for SiC-graphene composites (6) prepared by spark plasma sintering (SPS) prompted us to apply this method for synthesizing nanodiamond (ND) -reinforced ceramics as well. Although we expected that addition of NDs would increase the mechanical properties of the SiC ceramics, we found that during the SPS heat treatments NDs transformed to carbon nano-onions and nanographite and as a result, the composites showed quite poor mechanical properties. In order to understand the reason of this mechanical behavior, we studied the diamond-Si-SiC system between 1600 °C and 2000 °C in the function of ND and microcrystalline diamond (MD) addition as well as the quantity of Si bonding phase. We found that increasing sintering temperature induces intense graphitization and nano-onions, few-layered graphene and well-ordered graphite formations for the ND and MD composites at elevated temperature. Our high-resolution microscopy study demonstrated the occurrence of the previously erroneously identified 5H-SiC polytype in the samples prepared at 2000 °C. Regardless of the Si and diamond contents and quantities, SiC formation was not confirmed even at high temperature. We concluded the lack of such transitional phase prevents the fabrication of an improved SiC composite.

The new results (7) are in review in **Ceramics International**.

Use of the project results

Our new results are of fundamental interest in diamond research and the discovered nanomaterials are excellent candidates for technological applications. In particular, the peculiar nanostructures can be targeted for preparing materials with exceptional hardness as well as improved fracture toughness and ductility. Furthermore, they can be attractive for engineering the electronic conductivity as well as the optical and thermoelectric properties of diamond.

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Papers

1. **Németh P**, McColl Kit, Smith Rachael L, Murri M, Garvie LAJ, Alvaro M, Pécz B, Jones AP, Corà F, Salzmann CG, McMillan PF (2020) Diamond-Graphene Composite Nanostructures ***ACS Nano Letters*** 20/5, 3611-3619 (2020) **IF: 12.344***
2. **Németh P**, McColl K, Garvie LAJ, Salzmann CG, Murri M, McMillan PF (2020) Complex nanostructures in diamond ***Nature Materials*** 19, 1126–1131 (2020) **IF: 38.663***
3. **Németh P**, McColl K, Garvie LAJ, Salzmann CG, Pickard CJ; Corà F; Smith Rachael L, Mezouar M, Howard CA, McMillan PF Nanodiamonds exhibiting six- and twelve-fold symmetries. In preparation for ***Nature***.
4. **Németh P** and Garvie LAJ (2020) Extraterrestrial, shock-formed, cage-like nanostructured carbonaceous materials. ***American Mineralogist*** 105, 276–281 (2020). **IF: 2.922***
5. Murri M, Smith RL, McColl K, Hart M, Alvaro M, Jones AP, **Németh P**, Salzmann CG, Corá F, Domeneghetti MC, Nestola F, Sobolev NV, Vishnevsky SA, Logvinova AM and McMillan PF (2019) Quantifying hexagonal stacking in diamond, ***Scientific Reports*** 9, 10334, (2019). **IF: 3.998**
6. **Bódis E**, Cora I, **Németh P**, Tapasztó O., **Mohai M**, Tóth S., Károly Z., Szépvölgyi J. Toughening of silicon nitride ceramics by addition of multilayer graphene., ***Ceramics International*** 45, 4810-4816 (2019). **IF: 3.830**
7. **Bódis E**, **Cora I**, **Fogarassy Zs**, **Veres M**, **Németh P** High-temperature evolution of diamond – SiC composites. In review. Submitted to ***Ceramics International*** on 31.11.2020.

Talks in seminars and conferences

1. **Németh P.** Peculiar diamond nanostructures. Invited speaker at Nanolab Opening ceremony. Pannon University, Veszprém, October 2, 2018.
2. **Németh P.** What can we learn by studying minerals using transmission electron microscopy? Seminar talk at University of Innsbruck (Innsbruck, 2018.12.13).
3. **Németh P.** Gyémántok, amelyek hiányoztak a kristálytan óráról. 10. AKI Kiváncsi Kémikus kutatótábor megnyitó ünnepség. Meghívott előadó Július 2. 2018. (in Hungarian).

4. **Németh P**, Tóth S, Garvie LAJ, Jones AP, McMillan P Extrém körülmények különleges gyémántszerkezetei. 13. Téli Ásványtudományi Iskola. Veszprém, 2018. Január19-20 (in Hungarian).
5. **Németh P**, Tóth S, Koós M, Jones AP, McMillan P , Miller T, McGilvery C, Salzmann CG, Alvaro M, Murri M, Nestola F, Garvie LAJ Peculiar graphite-diamond grains in the impact-produced Popigai sample. Annual Meeting of HSM, Siófok, May 24-26, 2018 (in Hungarian).
6. **Németh P**, McColl K, Murri M, Smith RL, Garvie LAJ, Alvaro M, Pécz B, Jones AP, Corà F, Salzmann CG, McMillan PF: Különleges gyémánt-szerkezetekkel az újgenerációs gyémántrokon anyagok tervezése felé. AKI szemináriumi előadás (Budapest, 2020.09.08) (in Hungarian).

Abstracts in conferences

1. Tóth S, Pál MN, Himics L, Veres M and Koós M Spectral characteristics of Raman scattering measured on artificial and meteoritic diamond nanocrystals, Poster presentation in the 15th International Conference on Nanosciences & Nanotechnologies (NN18), 3-6 July 2018, Thessaloniki, Greece
2. Tóth S, Németh P, Garvie LAJ, Veres M and Koós M Nanodiamond with average grain size of 3-4 nm prepared by femtosecond laser pulses, Poster presentation in the 29th International Conference on Diamond and Carbon Materials, 2-6. September 2018, Dubrovnik, Croatia.
3. M. Miklós and I. Bertóti: Surface modification of carbon nanomaterials with graphitic and diamond structure by covalent attachment of nitrogen. Poster presentation at ECASIA conference in Dresden (Germany), September 14-20, 2019.
4. E. Bódis, Zs. Fogarassy, M. Veres, P. Németh: SIC/ NANO-DIAMOND CERAMIC COMPOSITES SINTERED BY SPS. Poster presentation at XVI ECerS Conference in Torino, June 16-20, 2019