Description of the results – 3rd stage of the project (January – December 2019)

Title of 3nd stage: Changing the aggregation state of impurities and defects in yellow-gold and dark cBN crystallites by thermochemical and/or irradiation treatments. Identification and characterization of the dispersed impurity states (continuation of the 2nd stage). Characterization by EPR and optical techniques of the dispersed atomic impurities and associated lattice defects in the cBN crystallites.

Estimated results of the research activity:

a. Procedure for the dispersion of the impurity aggregates in the yellow-gold (amber) and dark colored cBN crystallites (continuation of the 2nd stage).

b. Nature, structure and model of dispersion of the impurity aggregates in treated cBN crystallites.

c. Observation and identification of the dispersed impurities by EPR spectroscopy and microanalysis techniques.

d. Fundamental scientific information concerning the influence of the nature and concentration of impurities/defects on the optical and electrical properties of cBN crystals.

Results obtained in the present stage of the project:

a. We developed an original procedure for dispersing the aggregates/nanocrystals of α-Sn observed in the cBN crystallites, by eliminating the resulting surplus of Sn atoms through diffusion and oxidation at the surface of the host cBN crystallites. This process, which takes place in vacuum, at T= 950 ^{0}C, in about 4 hours, is accompanied by the oxidation of the extracted Sn atoms with the formation of residual, white powder deposits of SnO_2 on the cooler part of the fused silica ampoule/tube containing the annealed cBN crystallites. The resulting annealed cBN crystallites exhibit changes in their EPR spectra properties, as well as the disappearance of the aggregates/nanocrystals of α-Sn observed in the as-received dark cBN crystallites.

b. The data obtained from correlating the microstructural, microanalytical and multifrequency EPR measurements indicate that the dispersion of the aggregates of Sn is a thermally activated process which consists in their decomposition, followed by diffusion of the Sn atoms at the surface of the host cBN crystallites where they react with the residual oxygen gas forming white powder of nanocrystalline SnO_2 deposited on the cooler parts of the fused silica ampoule containing the cBN crystallites.

c. The analysis of the EPR spectra from the black Type 1 cBN crystallites, before and after the thermal treatment in vacuum of 4 hours at T= 950 ^{0}C, did evidence, besides the narrow, Lorentzian shaped EPR line, called A1, attributed to conduction electrons in the α-Sn nanocrystals, with g- value close to the free electrons g_e=2.0023 value, the presence of two, partly overlapping , broad lines called A2 and A3. While the narrow A1 line almost disappears in the annealed dark cBN crystallites, the broad

A2 and A3 lines do not change in a sensible manner their intensity, position and linewidth. Based on the analysis of their g-values and linewidth variation with temperature, we suggest a structural model based on a core Sn^{3+} ion with ns^1 - $^1S_{1/2}$ ground state, surrounded by oxygen impurity atoms and possible B vacancies, in two different configurations, in agreement with the microanalysis results.

d. The discovery of the of the presence of Sn aggregates in the dark cBN Type 1 crystallites, forming nanocrystals of α-Sn with topological Dirac 3D semi-metal properties represents a major scientific discovery. Firstly, because it is the first time that the presence of such nanocrystals with exotic properties are reported in a superhard material prepared at high temperature and high pressures comparable to those found deep in the earth mantle. Secondly, because it is for the first time that properties of a topological Dirac 3D semi-metal are reported for nanocrystals incorporated in a "bulk" crystalline host and not in thin films. The presence of these nanocrystals containing Dirac fermions with little known electron structure, is expected to lead to major changes in the electrical and optical properties, such as: giant mobility of the charge carriers, giant linear magneto resistance, or new quantum oscillations.

Presentation of the original results as communications at international scientific conferences and their publication as papers in internationally recognized (ISI) scientific journals.

The original scientific results obtained from the research activities performed in the frame of the present 3rd stage of the research project PN-III-P4-ID-PCE-2016-0079, have been presented as communications at international scientific conferences and published/submitted original papers in internationally recognized (ISI) scientific journals, as follows:

Publications (year 2019):

1. "Structure of defects in semiconductor crystalline cubic boron nitride. A microstructural and micro analytical investigation". L. C. Nistor, A. M. Vlaicu and S.V. Nistor, *Radiation Measurements*, **123**, 78-82 (2019).
2. "Presence and distribution of impurity defects in crystalline cubic boron nitride. A spectroscopic study". S. V. Nistor, L. C. Nistor, A. M. Vlaicu and A. C. Joita, *Radiation Measurements*, **123**, 21-25 (2019).
3. "Modular, high intensity monochromatic *in-situ* illumination set-up photo-active for investigating ESR photo-active centers in semiconductors". S. V. Nistor and A. C. Joita, *Applied Magnetic Resonance* (Springer), revised version, sent to the Editors by November 22, 2019.

Presentations at conferences (year 2019):

1. "Origin of the collective magnetism in cubic ZnS quantum dots doped with Mn^{2+} ions. From myths to the harsh reality." S. V. Nistor, The 16th International Conference on Nanosciences & Nanotechnologies, NN19, Thessaloniki, 2-5 July 2019 (invited).
2. "Nanostructured impurities in superhard crystalline cubic boron nitride", L. C. Nistor, S. V. Nistor, A. C. Joita, The 16th International Conference on Nanosciences & Nanotechnologies, NN19, Thessaloniki, 2-5 July 2019 (poster presentation).
3. "Nano aggregates of impurities in superhard cubic boron nitride crystals", A. C. Joita, S. V. Nistor, L. C. Nistor, R. F. Negrea, The 16th International Conference on Nanosciences & Nanotechnologies, NN19, Thessaloniki, 2-5 July 2019 (poster presentation).
4. "Analytical HRTEM/STEM study of impurity defects in cubic boron nitride crystals", L. C. Nistor, S. V. Nistor, R.F. Negrea, Conference of the Romanian Electron Microscopy Society, CREMS, Poiana Brasov, 23-25 October 2019 (oral presentation).
5. "Atomic impurity defects in crystalline cubic boron nitride semiconductor", S. V. Nistor, L. C. Nistor, A. C. Joita, Conference of the Romanian Electron Microscopy Society, CREMS, Poiana Brasov, 23-25 October 2019. (poster presentation)